PHILOSOPHICAL

TRANSACTIONS

OF THE

ROYAL SOCIETY

OF

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FOR THE YEAR MDCCCXLIV.

PART I.

LONDON:

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MDCCCXLIV.

ADVERTISEMENT.

THE Committee appointed by the *Royal Society* to direct the publication of the *Philosophical Transactions*, take this opportunity to acquaint the Public, that it fully appears, as well from the Council-books and Journals of the Society, as from repeated declarations which have been made in several former *Transactions*, that the printing of them was always, from time to time, the single act of the respective Secretaries till the Forty-seventh Volume; the Society, as a Body, never interesting themselves any further in their publication, than by occasionally recommending the revival of them to some of their Secretaries, when, from the particular circumstances of their affairs, the *Transactions* had happened for any length of time to be intermitted. And this seems principally to have been done with a view to satisfy the Public, that their usual meetings were then continued, for the improvement of knowledge, and benefit of mankind, the great ends of their first institution by the Royal Charters, and which they have ever since steadily pursued.

But the Society being of late years greatly enlarged, and their communications more numerous, it was thought advisable that a Committee of their members should be appointed, to reconsider the papers read before them, and select out of them such as they should judge most proper for publication in the future *Transactions*; which was accordingly done upon the 26th of March 1752. And the grounds of their choice are, and will continue to be, the importance and singularity of the subjects, or the advantageous manner of treating them; without pretending to answer for the certainty of the facts, or propriety of the reasonings, contained in the several papers so published, which must still rest on the credit or judgement of their respective authors.

It is likewise necessary on this occasion to remark, that it is an established rule of the Society, to which they will always adhere, never to give their opinion, as a Body,

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upon any subject, either of Nature or Art, that comes before them. And therefore the thanks, which are frequently proposed from the Chair, to be given to the authors of such papers as are read at their accustomed meetings, or to the persons through whose hands they received them, are to be considered in no other light than as a matter of civility, in return for the respect shown to the Society by those communications. The like also is to be said with regard to the several projects, inventions, and curiosities of various kinds, which are often exhibited to the Society; the authors whereof, or those who exhibit them, frequently take the liberty to report and even to certify in the public newspapers, that they have met with the highest applause and approbation. And therefore it is hoped that no regard will hereafter be paid to such reports and public notices; which in some instances have been too lightly credited, to the dishonour of the Society.

The Meteorological Journal hitherto kept by the Assistant Secretary at the Apartments of the Royal Society, by order of the President and Council, and published in the Philosophical Transactions, has been discontinued. The Government, on the recommendation of the President and Council, has established at the Royal Observatory at Greenwich, under the superintendence of the Astronomer Royal, a Magnetical and Meteorological Observatory, where observations are made on an extended scale, which are regularly published. These, which correspond with the grand scheme of observations now carrying out in different parts of the globe, supersede the necessity of a continuance of the observations made at the Apartments of the Royal Society, which could not be rendered so perfect as was desirable, on account of the imperfections of the locality and the multiplied duties of the observer.

A List of Public Institutions and Individuals, entitled to receive a copy of the Philosophical Transactions of each year, on making application for the same directly or through their respective agents, within five years of the date of publication.

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A List of Public Institutions and Individuals, entitled to receive a copy of the Astronomical and Magnetic Observations made at the Royal Observatory at Greenwich, on making application for the same directly or through their respective agents, within two years of the date of publication.

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ROYAL MEDALS.

HER MAJESTY QUEEN VICTORIA, in restoring the Foundation of the Royal Medals, has been graciously pleased to approve the following regulations for the award of them:

That the Royal Medals be given for such papers only as have been presented to the Royal Society, and inserted in their Transactions.

That the triennial Cycle of subjects be the same as that hitherto in operation: viz.

1. Astronomy; Physiology, including the Natural History of Organized Beings.
2. Physics; Geology or Mineralogy.
3. Mathematics; Chemistry.

That, in case no paper, coming within these stipulations, should be considered deserving of the Royal Medal, in any given year, the Council have the power of awarding such Medal to the author of any other paper on either of the several subjects forming the Cycle, that may have been presented to the Society and inserted in their Transactions; preference being given to the subjects of the year immediately preceding: the award being, in such case, subject to the approbation of Her Majesty.

The Council propose to give one of the Royal Medals in the year 1844 for the most important unpublished paper in Mathematics, communicated to the Royal Society for insertion in their Transactions after the termination of the Session in June 1841, and prior to the termination of the Session in June 1844.

The Council propose also to give one of the Royal Medals in the year 1844 for the most important unpublished paper in Chemistry, communicated to the Royal Society

for insertion in their Transactions after the termination of the Session in June 1841, and prior to the termination of the Session in June 1844.

The Council propose to give one of the Royal Medals in the year 1845 for the most important unpublished paper in Astronomy, communicated to the Royal Society for insertion in their Transactions after the termination of the Session in June 1842, and prior to the termination of the Session in June 1845.

The Council propose also to give one of the Royal Medals in the year 1845 for the most important unpublished paper in Physiology, including the Natural History of Organized Beings, communicated to the Royal Society for insertion in their Transactions after the termination of the Session in June 1842, and prior to the termination of the Session in June 1845.

The Council propose to give one of the Royal Medals in the year 1846 for the most important unpublished paper in Physics, communicated to the Royal Society for insertion in their Transactions after the termination of the Session in June 1843, and prior to the termination of the Session in June 1846.

The Council propose also to give one of the Royal Medals in the year 1846 for the most important unpublished paper in Geology or Mineralogy, communicated to the Royal Society for insertion in their Transactions after the termination of the Session in June 1843, and prior to the termination of the Session in June 1846.

The Council propose to give one of the Royal Medals in the year 1847 for the most important unpublished paper in Mathematics, communicated to the Royal Society for insertion in their Transactions after the termination of the Session in June 1844, and prior to the termination of the Session in June 1847.

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PHILOSOPHICAL TRANSACTIONS.

I. *Additional Researches on the Electrolysis of Secondary Compounds.* By J. Frederic Daniell, *Esq., D.C.L., For. Sec. R.S., Prof. Chem. in King's College, London, and* W. A. Miller, *Esq., M.D., Dem. of Chem. in King's College, London.*

Received February 15,—Read February 25, 1844.

THE authors of the following paper having agreed to work together upon the subject of the electrolysis of secondary compounds as opened by one of them, in two letters addressed to Dr. Faraday, and honoured with a place in the Philosophical Transactions for 1839 and 1840, have arrived at some results, which probably will not be without interest to the Royal Society, and which they have now the honour to communicate.

In the two papers just alluded to, the following points were established. *First.* When aqueous solutions of the neutral metallic salts are exposed to the action of the voltaic current, they are invariably decomposed. When the metal is one of that class which does not decompose water at ordinary temperatures, it is precipitated in the metallic state at the platinode: when it is of the class which does decompose water, its oxide, with an equivalent proportion of hydrogen, appears at the same electrode. The acid at the same time is set free at the zincode, accompanied by an equivalent proportion of oxygen. *Second.* When these results are compared with those of an independent voltameter in the same circuit, it is found that a certain proportion of the force which resolves a single equivalent of a *simple** electrolyte into its anion and cation, produces the resolution of a full equivalent of the *complex* electrolyte into a simple metallic cation and a compound anion. *Third.* When aqueous solutions of ammoniacal salts are electrolysed, similar results are obtained; but instead of a simple metal being disengaged at the platinode, an equivalent of ammonia, accompanied in all cases by an equivalent of hydrogen, appears at the platinode. *Fourth.* We are thus entitled to conclude that in the electrolysis of complex electrolytes, different

* By a simple electrolyte is meant one containing only two elementary substances, being the simplest form of matter capable of electrolysis.

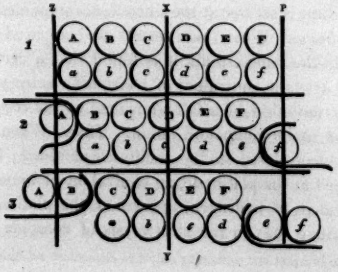
elements travel together under the influence of the voltaic current as compound anions and cations, or as *iso-electric* bodies; that is, groups which are equivalent to each other, and to simple ions, in their relations to the electric forces.

One of the most interesting results of this investigation, was the independent confirmation which it afforded of two celebrated hypotheses, viz. that of Davy regarding the constitution of aqueo-acids, and the general analogy in the constitution of salts, whether derived from oxyacids or hydro-acids; and that of Berzelius concerning the constitution of ammonium.

It was with a view to extend our knowledge of such iso-electric groups, and to trace their connexion with chemical radicles, that we commenced our experiments.

Before we enter upon their detail, it will be best to make a few remarks upon the mode of measuring their results, which has been adopted. It is founded upon the undoubted law of definite electric action; and we have indifferently taken the amount of the ions disengaged at either or both the electrodes by the primary action of the current, or the secondary action of the elements. But there is another mode of effecting this purpose, by a diaphragm cell, in which the products of electrolysis may be kept separate; a method founded upon the hypothesis, that the voltaic decomposition of an electrolyte is not only effected by the disengagement of its anion and cation at their respective electrodes, but by the equivalent transfer of each to the electrodes; so that the measure of the quantity of matter translated to either side of the diaphragm might be taken as the measure of the electrolysis.

This was the mode which was necessarily adopted in the investigation before adverted to, where attempts were made to compare the results of the electrolysis of aqueous solutions of acids* and alkalies† with the simultaneous decomposition of saline solutions. One circumstance, however, was then overlooked, which it is necessary to attend to in making the comparison, viz. that the *disengagement* of whole equivalents of the ions at the electrodes is only accompanied, upon the hypothesis assumed, by the actual *transfer* of half an equivalent to *either* side. This will clearly appear from the following diagram.



* First Letter, p. 108.

† Second Letter, p. 216.

Let A, B, C, &c. in the preceding diagram represent a series of particles of chlorine, *a*, *b*, *c*, &c. a series of particles of potassium in combination with the particles of chlorine in the row above them, X, Y a central line or diaphragm, and Z and P the electrodes. If 1 represent the arrangement before the current passes, the particles A and *a*, B and *b*, &c. being combined to form compound particles of chloride of potassium, 2 would represent the arrangement after a single equivalent of each ion had been disengaged at the electrodes. Each particle would thus necessarily have moved forward half a step, combining with the next adjacent particle, so that B *a*, C *b*, D *c*, &c. would now form the chain between the electrodes. If another equivalent be now supposed to be set free at each electrode, one particle of each ion would have passed the central line, one equivalent would thus be *transferred*, whilst two had been *disengaged*, as in fig. 3.

In the instances above referred to, the transfer of one quarter of an equivalent represented half of an equivalent of the hydrates respectively electrolysed. Little stress however need be laid upon this correction, inasmuch as we shall presently show that the hypothesis upon which it is founded, although generally received, is itself destitute of foundation.

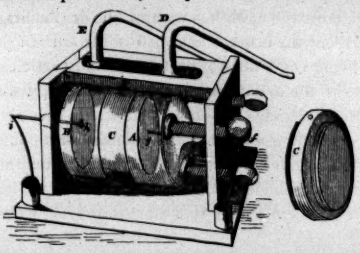
1. Our first object was to ascertain more clearly than had yet been done, the influence of water in the aqueous solution of an electrolyte, by comparison with the results of the electrolysis of the same compound when in the state of igneous fusion. It had been already determined, that with regard to the *chlorides* no difference occurred, and that the amounts of chlorine evolved in the same circuit from *fused* chloride of lead *, and from *dissolved* chloride of sodium and muriate of ammonia, were the same †. In the last case, ammonia and hydrogen were evolved at the platinode in equivalent proportions to the chlorine at the zincode. Here a compound cation (NH_4) was separated from an elementary anion.

When *nitrate of silver* in solution is subjected to electrolysis, the simple cation, silver, separates from the compound anion (NO_6), and upon substituting the *salt in a state of fusion*, for the solution, we obtained the same result. No gas was evolved, but *crystallized metallic silver* was deposited upon a silver platinode, which gradually increased in length, as it was slowly withdrawn from the liquid salt, just as in the analogous experiment with fused chloride of silver, devised by Dr. Faraday. Nitrous fumes were at the same time given off from the platinum zincode in abundance. From these experiments it is evident that neither the grouping of a compound cation, nor of a compound anion, is necessarily altered by water in the transit to their respective electrodes.

2. We now turned our attention to that most interesting group of salts, the *phosphates*, which has been so ably discussed by Professor Graham; not without hopes of confirming by electrolysis the beautiful theory of their constitution, which he has

* First Letter, p. 108. † Ibid. p. 110.

derived from considerations purely chemical. *The double diaphragm cell* which we chiefly employed in these experiments, is represented in the annexed wood-cut.



A and B are the two halves of a stout glass cylinder, accurately ground so as to fit with shoulders liquid tight. C is a hollow ring of glass, also ground on either side, with a flat shoulder to fit against the two half cylinders, which are pressed home by the screws. Each side of the ring is furnished with a rim, which is grooved to admit of a thin piece of bladder being tied over it to form a kind of drum; at K is a small hole to admit of the cavity being filled with a liquid. D and E are two bent tubes, fitted to the two half cylinders for collecting the gases evolved in the experiments. *g* and *h* are two circular platinum electrodes connected by wires, *i*, *f* (passing through corks in the necks of the half cylinders), with the battery. The apparatus when adjusted forms three compartments, each of which may be filled with the same or a different liquid, and the whole may be supported on a light frame of wood.

We will not attempt to describe the particulars of every experiment referred to in the following pages, for their number is very great, and their details would be both tedious and useless; we will only select some of the principal, in the results of which we can trace no ambiguity; and have no doubt we shall obtain credit for every care in determining the purity of the substances which we employed, and in making the various analyses which were required.

(*a.*) A strong solution of *tribasic phosphate of soda and water* ($2NaO, HO, P_2O_5$) (rhombic phosphate) was placed in the platinode cell of the diaphragm apparatus; the centre cell and the zincode cell were both charged with a dilute solution of soda ($\frac{1}{48}$). The power of twenty cells of the small constant battery was transmitted through it, oxygen was evolved at the zincode, and in thirty-seven minutes 48 cubic inches of hydrogen were collected from the platinode; the experiment was then stopped and the solutions examined.

The liquid from the zincode cell was carefully neutralized with nitric acid, and then gave a copious yellow precipitate with nitrate of silver, soluble in nitric acid, and in ammonia, the well-known characters of the tribasic phosphate of silver ($3AgO, P_2O_5$). The solution in the platinode cell had become much more alkaline than at first, but when neutralized with nitric acid, gave a similar yellow precipitate with

nitrate of silver. There could be no doubt therefore that *tritoxyphosphion* (or the radicle of the tritohydrate of phosphoric acid) had travelled to the zincode. The experiment was more than once repeated with unvarying results.

(*b.*) A solution of *tribasic phosphate of soda* ($3NaO, P_2O_5$) (sub-phosphate) was substituted in the same arrangement for the rhombic phosphate, and, after the action of the battery, on neutralizing the liquid in the zincode cell, a similar copious yellow precipitate was obtained from nitrate of silver.

(*c.*) To complete the series of tribasic phosphates in which different bases are substituted for each other, a solution of the *phosphate of soda, ammonia and water* $\left(\begin{matrix} NaO \\ NH_4O \\ HO \end{matrix}\right\} P_2O_5)$ (microcosmic salt), was subjected in the same manner to electrolysis, the zincode cell being charged with solution of soda; the solution in the zincode cell became acid to the test of litmus, and produced an abundant yellow precipitate in solution of nitrate of silver; proving that it was the tribasic acid which had travelled as before.

(*d.*) A similar arrangement was made with a solution of *dibasic phosphate* (pyrophosphate) of soda ($2NaO, P_2O_5$). Hydrogen and oxygen in equivalent proportions were respectively given out at the platinode and zincode, and the process was carried on to the same extent as before. The solution at the zincode after electrolysis was neutralized by nitric acid. When tested with solution of nitrate of silver, a copious white precipitate was formed, indicating that in this case *deutoxyphosphion* (or the radicle of the deuto-hydrate of phosphoric acid) had been transferred to the zincode.

(*e.*) A solution of *monobasic phosphate* (NaO, P_2O_5) (metaphosphate) was subjected to electrolysis under the same circumstances. The solution in the zincode cell was now found to be strongly acid instead of alkaline; when added to a solution of albumen it immediately coagulated it; and with nitrate of silver and nitrate of baryta it produced the characteristic gelatinous white precipitates, which are distinctive of the monobasic phosphates of those bases.

It was thus fully established by these experiments, and confirmed by their repetition, that the three hydrates of the phosphoric acid constitute three essentially distinct acids, which may be expressed as follows:—

$H + P_2O_6$ proto-hydrate,
$H_2 + P_2O_7$ deuto-hydrate,
$H_3 + P_2O_8$ trito-hydrate,

and that when disengaged from their corresponding saline compounds by the power of the voltaic current, they travel as three distinct *oxyphosphions* in the circuit. This view, which cannot be doubted as arising from the properties of the acids so disengaged, derives confirmation from the observation that the quantity of acid transferred from the monobasic phosphate of soda was so much greater for the same amount of hydrogen disengaged, than from the dibasic and tribasic salts of the same base.

We had thus the gratification of establishing by independent testimony the correctness of Professor GRAHAM's theory of the phosphates, and it is with pleasure we also observe that his view of the basic character of water in certain saline compounds is confirmed by the results of the electrolysis of the three tribasic phosphates; from all of which the same acid was separated, notwithstanding that in two instances water obviously constituted one of the three equivalents of base. In our corresponding view, one of the three equivalents of metals was represented by hydrogen.

3. Next in natural order seems to stand the inquiry whether the salts of other tribasic acids would afford analogous results to those of the tribasic phosphates.

(*f.*) For this purpose we selected the *tribasic arseniate of potassa and water* ($KO, 2HO, As_2O_5$) (binarseniate), the platinode cell was charged with a solution of the salt, and the zincode cell and connecting cell with solution of potassa. The combination was found to conduct very well, and oxygen and hydrogen were given off at their respective electrodes. The solution in the platinode cell assumed a grayish appearance, but there was no smell of arseniuretted hydrogen, nor was any arsenic deposited upon the electrode. The solution had become neutral to test paper. The liquid in the zincode cell was carefully neutralized by acetic acid, and afterwards produced in solution of nitrate of silver, the characteristic brick-red precipitate of the arseniate of silver ($3AgO, As_2O_5$), so that there could be no doubt that the *tritoxarsenion* had travelled into the zincode cell.

The complicated secondary actions which take place in the electrolysis of organic compounds, and which we hope to make the subject of future communications, induce us to abstain at present from extending this part of our inquiry to the organic acids.

4. An inquiry of considerable interest now claims our attention, viz. the electrolysis of salts whose acids, having the same elementary radicle as some of those which have been already examined, are in an inferior degree of oxygenation: such are the arsenites and sulphites.

(*g.*) A solution of *arsenite of potassa* (KO, As_2O_3) was carefully prepared (by dissolving single equivalents of arsenious acid and bicarbonate of potassa in boiling water), and placed in the platinode cell of the diaphragm apparatus; the connecting cell and the zincode cell were both charged with solution of potassa. During the electrolysis oxygen was given off at the zincode, but an equivalent of hydrogen was not obtained at the platinode, the electrode being covered with metallic arsenic, which was deposited in such abundance as speedily to render the liquid opake; there was no smell of arseniuretted hydrogen. This diffusion of the metal reduced by secondary action, throughout the solution, contrasts well with the compact manner in which metals are deposited, which, like copper from the neutral sulphate, are thrown down by direct voltaic action. The zincode solution was exactly neutralized by acetic acid; after which a yellow precipitate of the arsenite of silver was produced on adding nitrate of silver.

In this case, as in that of the arseniate just described (3. *f.*), free oxygen was evolved, but the corresponding hydrogen arising from the secondary action of the potassium at the other electrode was taken up in the reduction of the arsenious acid in contact with which it was evolved. No such reduction of the arsenic acid was effected.

It might have been anticipated that the oxygen in travelling with the arsenious acid to the zincode would have combined with it, and formed a portion of arsenic acid; but no such result took place: and it must be remarked, that two equivalents of oxygen instead of one would be required fully to oxidate the whole. We must, therefore, conclude that $As_2 O_3 + O$ constitute what we may for the present distinguish as a *sub-oxarsenion*.

The experiment was repeated, by charging all the three cells of the apparatus with the solution of the salt, when oxygen was given off from the zincode as before, and arsenious acid was deposited in white crystals.

(*h.*) The *carbonates* and *oxalates* may be compared together in the same point of view as acids of the same radicle in different states of oxygenation. It has been already stated that in the electrolysis of the former, carbonic acid and oxygen were found to be given off at the zincode in equivalent proportions to the alkali and hydrogen at the platinode; proving those salts to be *oxy-carbions* of the respective metals*. When oxalate of ammonia was treated in the same way, carbonic acid alone was evolved at the zincode, and ammonia with hydrogen at the platinode*. Here the *oxalion* (or sub-oxycarbion) contains the elements of two equivalents of carbonic acid $(C_2 O_3 + O) = 2(CO_2)$. In numerous repetitions which we now made of these experiments, we found that although in the electrolysis of oxalate of ammonia $(C_2 O_3 + O)$ was always exactly evolved, yet that it was not invariably in the form of carbonic acid, but in different proportions of oxalic acid with free oxygen and carbonic acid. It was thus proved that the burning of the oxalic acid into carbonic acid by its associated oxygen was a secondary process, and that the $(C_2 O_3 + O)$ which travelled in the circuit was in some way different from $2(CO_2)$.

(*i.*) A similar comparison was then made between the *sulphites* and *sulphates*. In the electrolysis of the latter, it has been shown that sulphuric acid with an equivalent of oxygen (which is evolved) travels to the zincode†. To determine the results of the former, all the cells of the diaphragm apparatus were charged with sulphite of potassa, and a voltameter was included in the circuit; hydrogen was given off from the platinode in exact proportion to that from the voltameter; but no oxygen was evolved from the zincode.

The experiment was by itself ambiguous, for it did not determine whether $(SO_2 + O)$ travelled as SO_3, or whether sulphuric acid was formed at the zincode by the secondary action of the oxygen upon the sulphurous acid. Judging from the analogy of the preceding instances, it is most probable that the oxygen with which the sulphurous acid is associated in the *sub-oxysulphion* is in a different state from that of the third

* Second Letter, p. 222. † First Letter, pp. 107 *et seq.*

equivalent in dry sulphuric acid, and that the sulphuric acid evolved at the zincode in the last experiment is the result of secondary action. Some sulphurous acid was evolved in the zincode cell, which doubtless arose from the action of the sulphuric acid upon the sulphite in contact with which it was produced.

(*k*.) The experiment was varied by substituting *hyposulphite of soda* (NaO, S_2O_2) for the sulphite, and with analogous results. Hydrogen was given off abundantly at the platinode, but no gas was evolved at the zincode. There was a strong odour of sulphurous acid at the latter, with a gradual deposition of sulphur. This doubtless arose from the secondary action of the sulphuric acid, which was first formed upon the salt with which it was in contact, by which hyposulphurous acid was disengaged, and immediately decomposed. The constitution of the hyposulphite being (NaO, S_2O_2), that of the corresponding sub-oxysulphion would be S_2O_3, which if burnt at the zincode would produce $S + SO_3$.

5. We now proceeded to apply the method of electrolysis to solve a problem of the same nature as that of the three hydrates of the phosphoric acid, viz. to determine the exact relations of the *yellow and red ferrocyanides of potassium*. It is well known that two views have been taken of the constitution of these two salts: the first represents the yellow salt as a *ferrocyanide of potassium* ($K_2, Fe\,Cy_3$), and the red salt as a *subsesquiferrocyanide* of potassium $K_3 + 2(Fe\,Cy_3)$. The second view represents the two salts as compounds of those metals with two distinct radicles, the former denominated *ferrocyanogen* ($Fe\,Cy_3$), the latter *ferridcyanogen* ($Fe_2\,Cy_6$). The ferrocyanogen forms a dibasic acid with hydrogen ($H_2, Fe\,Cy_3$), the salts of which are produced by the substitution of two equivalents of the metals for the two equivalents of hydrogen; and the ferridcyanogen forms with hydrogen a tribasic acid ($H_3 + Fe_2Cy_6$), with a similar substitution of three equivalents of the metals in their different salts. The real chemical difference, therefore, between the yellow and red ferrocyanides of potassium, consists in the latter containing half an equivalent less of potassium than the former; and so with the other salts from the two classes the metallic elements are in the proportion of 1 to $1\frac{1}{2}$.

Now Mr. Porrett*, the discoverer of the hydroferrocyanic acid (or as he proposed to call it, the ferro-chyazic acid), long since determined that it travelled in the voltaic circuit by the electrolysis of its salts, to the zincode, the iron accompanying the cyanogen in this transfer, contrary to what might previously have been expected. The question which we now proposed to determine was, whether *ferridcyanogen* as well as *ferrocyanogen* would thus constitute a distinct anion under the directing influence of the battery.

Mr. Smee† has already determined that the subsesquiferrocyanide of potassium may be formed from the ferrocyanide by the action of the voltaic battery; and has even proposed the process for obtaining the red salt upon a large scale. He, however, explains the change by the action of *nascent oxygen*, which he supposes to be evolved

* Philosophical Transactions, 1814, p. 529.

† Philosophical Magazine, xvii. p. 196.

at the zincode. He observes, "that one equivalent of the yellow *ferrocyanate* is decomposed, the *free potash* travels one way, and the *hydroferrocyanic* acid the other. The oxygen unites with the hydrogen of the acid and sets ferrocyanogen at liberty; this again unites with an equivalent of the *ferrocyanuret of potassium* to form the *ferrosesquicyanuret*." It is evident from this, that this gentleman entertains a very different notion of the steps of the electrolysis to that which we feel justified in supporting, and that therefore he has failed to place it in the point of view to which we propose to adhere.

(*l.*) We commenced our inquiry by carefully repeating Mr. SMEE's experiment in a diaphragm cell, charged throughout with a strong solution of the *yellow ferrocyanide of potassium*. A voltameter was included in the circuit, and the power of twenty cells of the small constant battery was employed. Gas was evolved at the platinode, which was tested and found to be pure hydrogen; it was in equivalent proportion to the gases in the voltameter. No gas was at first evolved at the zincode, but the solution in that cell became gradually red, particularly at the surface. When 4 inches of hydrogen had been collected at the platinode a slight disengagement of gas commenced at the zincode, which continued, and proved to be oxygen, and was in the proportion of one-third of the gas from the platinode. After 16 cubic inches had been collected from the platinode, we stopped the experiment and examined the results.

The platinode solution was much paler than before, and was alkaline. The zincode solution was deep green and acid, and the zincode plate was covered with a slight film of Prussian blue. Crystals of the red ferrocyanide separated from the zincode solution by spontaneous evaporation, and when the evaporation was complete, a radiated mass of a purplish-brown colour was obtained: on solution a small quantity of Prussian blue remained, and the solution had lost its acid reagency. The addition of acetate of lead to the solution produced but a scanty precipitate, proving the quantity of yellow ferrocyanide remaining in it to be but small.

The explanation of these results is, we think, sufficiently obvious. Ferrocyanogen was doubtless transferred to the zincode, and potassium to the platinode, the former combined with a portion of the ferrocyanide to form the subsesquiferrocyanide; the process being accelerated by the abstraction of a portion of the potassium passing over to the platinode, where by its reaction upon the water of the solution it was converted into potassa with the evolution of hydrogen. As the process proceeded more ferrocyanogen was given off at the zincode than could be absorbed by the yellow salt; and it consequently began to react upon the water, becoming converted by the abstraction of its hydrogen into hydroferrocyanic acid, its oxygen being evolved. The acid reaction is thus accounted for, as well as the deposition of Prussian blue, from the well-known spontaneous decomposition of the acid.

(*m.*) This experiment was several times repeated with variation of the quantities, but with substantially the same results. The evolution of oxygen from the zincode

was hastened by narrowing the dimensions of the electrode, which thus presented a smaller surface for the reaction of the ferrocyanogen upon the ferrocyanide. When the process was continued for a long time, yellow crystals of the ferrocyanide were formed in the platinode cell. Upon subsequent trial it was found that a strong solution of potassa produced a similar deposit, under ordinary circumstances, in a solution of the yellow salt. It will probably be objected, that although the red ferrocyanide is thus obviously formed by secondary action, yet where once formed it may be capable of decomposition as an electrolyte, in which ferridcyanogen acts as the anion. The following experiment however is decisive against such a view.

(*n.*) The diaphragm cell was charged throughout with a strong solution of *the red salt*, the purity of which had been tested. The solution was deep green by reflected light, but red by transmitted light. The power of the same constant battery was applied to it, and the platinode solution very quickly changed its colour and became yellow. When 5·75 cubic inches of hydrogen had been collected from the platinode the yellow colour was perfectly pure; the action was then stopped. The liquid at the zincode was of a very dark brown-green colour, and strongly acid, it had a pungent peculiar smell, the liquid soon became perfectly opake, and one cubic inch of oxygen was collected from the zincode. Though the colour of the two solutions in the electrode cells had undergone such marked changes, the colour of that in the intermediate cell remained unaltered. The liquid from the platinode cell yielded on evaporation tabular crystals of the yellow ferrocyanide, and when hydrate of potassa was added to the zincode solution, a yellow colour was developed.

Here then we obviously have the converse results of the last experiments; or the formation of ferrocyanide of potassium from subsesquiferrocyanide by the abstraction of half an equivalent of ferrocyanogen transferred from the platinode to the zincode.

(*o.*) Could a doubt remain with regard to the conclusion to be derived from these experiments, it must be removed by the results of the following arrangement. The zincode cell was filled with a dilute solution of potassa, and the connecting cell with the same. The platinode cell was charged with a strong solution of the red ferrocyanide. This solution previously to the commencement of the experiment gave no blue solution with perchloride of iron. The liquid in the zincode and connecting cells speedily became yellow, and after a short time the solution in the platinode cell also became yellow. All the solutions were now found to contain the yellow ferrocyanide. Thus it was quite clear that no such compound as ferridcyanogen travelled from the red salt when exposed to electrolysis, but that the red salt was converted into the yellow by the abstraction of ferrocyanogen from the platinode, which ferrocyanogen being transferred to the zincode, there formed with the potassium presented to it by electrolysis the same yellow ferrocyanide.

In order to extend further our knowledge of the electrolysis of this class of secondary compounds, the following experiments were made:—

(*p.*) A diaphragm apparatus was charged with a strong solution of *cyanide of po-*

tassium (K, Cy) in the platinode cell, and a solution of potassa in the zincode and connecting cells. The arrangement conducted well; gas was given off from both electrodes, and cyanide of potassium formed in abundance in the zincode cell. Hydrogen must therefore have been given off at the platinode by the oxidation of the potassium evolved, and oxygen at the zincode by the deoxidation of potassa under the influence of the current in the formation of the cyanide of potassium.

(*q*.) The apparatus was charged throughout with solution of cyanide of potassium, and subjected to the current. Gas was given off as before at the platinode; but at first none from the zincode. The liquid in the zincode cell gradually became of a deep brown colour, and the electrode itself was coated with a deep brown matter, which was easily washed off. In the latter part of the operation gas was also evolved in small quantity at the zincode. The solution smelled strongly of hydrocyanic acid, of which, by the proper tests, it was found to contain a considerable quantity. There can be no doubt that the brown matter which was abundantly formed was *paracyanogen*, which is soluble in the alkaline solution of the cyanide of potassium, and which must have been produced either by the spontaneous decomposition of the hydrocyanic acid, or in a way something analogous to the formation of the red ferrocyanide of potassium from the yellow by the absorption of an additional quantity of ferrocyanogen.

(*r*.) A diaphragm apparatus was charged throughout with *sulphocyanide of potassium* ($K, S_2 Cy$). Upon the first application of the current the action was brisk, but soon declined, and when $5\frac{1}{2}$ cubic inches of gas had been collected from the platinode and $1\frac{1}{2}$ cubic inch from the zincode it ceased. There was a copious orange-coloured deposit in the zincode cell and upon the plate which interrupted the progress of the electrolysis; no particular odour was perceptible in either of the cells. The liquid filtered from the zincode became turbid by exposure to the air, and deposited more of the yellow compound. The clear liquid was again subjected to the current, which it transmitted readily, and with the same phenomena as before. There could be little doubt that *sulphocyanogen* was the anion transferred in this experiment. This part of our subject still presents a tempting field for investigation, from which however we were for a time diverted by an important class of facts which next fell under our observation; we have however since returned to the study, and are at present engaged in researches upon the cobaltocyanides, and other double cyanides, the results of which we hope ere long to lay before the Society.

6. We were purposing to follow up the examination of the double salts by the electrolysis of other classes of these compounds, when we were stopped by the occurrence of a new order of phenomena, which it was necessary to turn aside and examine as affecting the very foundation of the process which we were employing. In our examination of the phosphates, our plan had been to transfer by electrolysis the acid of the salt placed in the platinode cell into a solution of potassa placed in the zin-

code cell for its reception, and then to determine its quantity and its properties from those of the salt which was formed by secondary combination.

The arrangement which we now made was to place the salt at the zincode with the view of passing its bases into an acid at the platinode. We commenced our experiments with the double sulphates with the view of comparing the different hydrates of the sulphuric acid with the hydrates of the phosphoric acid already examined, and throwing more light upon the results of the electrolysis of the dilute acid.

(*s.*) Some pure *sulphate of potassa and copper* ($CuO, SO_3, + KO, SO_3$) was carefully prepared, and its solution placed in the zincode and connecting cells of the diaphragm apparatus: the platinode cell was charged with dilute sulphuric acid, the current of twenty cells of the battery was transmitted through the arrangement until 48 cubic inches of hydrogen had been collected from the platinode, and 23·5 cubic inches of oxygen from the zincode (about one equivalent in grains), when the process was stopped. The platinode solution was perfectly colourless with a very slight deposit of copper upon the platinode, amounting only to 0·1 grain. It was evaporated to dryness in vapour of ammonia, and the residue was perfectly white sulphate of potassa, which weighed 21 grains. It was entirely soluble in water: and ammonia did not produce the slightest blue colour in its solution. The liquids of the zincode and connecting tubes together required 51 grains of dry carbonate of soda to neutralize the free acid. Now, it will be observed, that the sulphate of potassa was only one grain less than a quarter of an equivalent, which considering the nature of the processes by which these quantities were determined, will appear a very near approximation; and we may take the results of the electrolysis to have been as follows:— For one equivalent of force as measured by the gases evolved at the zincode and platinode, half an equivalent of oxysulphion of potassium (sulphate of potassa) was decomposed (as measured by the quarter equivalent potassium transferred), and half an equivalent of oxysulphion of hydrogen (aqueous sulphuric acid): for it will be observed, as most remarkable, that the quantity of copper transferred was perfectly insignificant.

Upon the view of the principle of electrolysis hitherto commonly admitted, viz. definite decomposition with equivalent and opposite transfer of the elements or radicles of the compound to the opposite electrodes of the battery, these results were sufficiently perplexing: but our perplexity increased as we proceeded; and it was not till after we had expended an incredible amount of labour in testing different hypotheses of various resistances and opposing forces, supposed to be developed in these complicated cases, that we thought of questioning the principles themselves. These abortive attempts we shall not, of course, obtrude upon the Society, but proceed to select such experimental evidence as may be sufficient to establish, in as concise a manner as possible, the conclusions to which we have arrived.

(*t.*) A solution of *sulphate of alumina and potassa* (alum) ($Al_2O_3, 3SO_3$) + (KO, SO_3)

was subjected to exactly the same treatment as the preceding double salt, and the results were precisely similar. 48 cubic inches of hydrogen were collected from the platinode. When ammonia was added in excess to the solution in the platinode cell no precipitate was produced, which proved the absence of alumina. Evaporated to dryness, the saline residue was ignited, and weighed 21 grains. It was sulphate of potassa, and the amount, as before, was within one grain of the quarter of an equivalent.

(*u.*) Some of the double *sulphate of magnesia and potassa* ($MgO, SO_3, + KO, SO_3$) was carefully prepared, and submitted in solution to the same treatment. After 48 cubic inches of hydrogen had been collected the platinode solution was evaporated to dryness, and left a saline residue of 36·6 grains. This was redissolved and treated with carbonate of potassa. A precipitate of carbonate of magnesia was thus obtained, which was reconverted into sulphate, and weighed 3·8 grains; this was equivalent to 0·76 grain of magnesium, to which must be added 0·24 grain recovered from the wash water by means of phosphate of ammonia, making the total quantity of magnesium which had passed over to the platinode 1·0, or about $\frac{1}{12}$th of an equivalent. Deducting the total amount of sulphate of magnesia, 4·98 grains, from the mixed sulphates, 36·6 grains, we have 31·62 as the amount of the sulphate of potassa.

Thus it appeared that the three bases, alumina, magnesia, and oxide of copper, or their metals, when in combination with sulphuric acid and potassa, refused to travel from the zincode to the platinode under the influence of the voltaic current into an acid with which they were capable of forming an immediate and soluble combination. Could it be that the same results might follow from the electrolysis of the single salts of the same acid?

(*w.*) Some pure *sesquisulphate of alumina* ($Al_2 O_3, 3SO_3$) was prepared by precipitating alum with excess of ammonia, thoroughly washing the precipitate and redissolving it in sulphuric acid, with the aid of heat. An excess of alumina was left, from which the liquid was separated by filtration. It was then evaporated till it solidified upon cooling. The mass was subjected to pressure in calico, and the dry salt dissolved in water.

The zincode and connecting cells of the diaphragm apparatus were then charged with the solution, and the platinode cell with dilute sulphuric acid. The arrangement conducted well, and in half an hour 13 cubic inches of oxygen were collected from the zincode. The process was then stopped, and on supersaturating the liquid at the platinode with ammonia, the slightest possible trace of alumina was precipitated.

Thus it again appeared that the electrolysis was carried on without the transfer of the base or its metal to the platinode.

Was the peculiar constitution of this salt as a *sesqui* compound concerned in any way in this result?

(*x*.) A salt of the same order, viz. the *sesquisulphate of iron* (Fe_2O_3, $3SO_3$), was prepared with great care, and its solution treated exactly in the same way as the last. It conducted well, and 13 cubic inches of oxygen were collected from the zincode in twenty-eight minutes. On neutralizing the liquid of the platinode cell with ammonia, very slight traces of sesquioxide of iron appeared. The sesquioxide of iron had therefore resisted the transfer as well as the sesquioxide of aluminum.

(*y*.) We next tried salts of the more ordinary constitution of single equivalents of acid and base. The zincode and connecting cells were charged with solution of *sulphate of copper* (CuO, SO_3), and the platinode cell with dilute sulphuric acid. The combination conducted well, 23·6 cubic inches of oxygen were collected from the zincode, and an equivalent of hydrogen from the platinode; but the platinode plate was scarcely covered with a very thin film of copper, the metal not having been transferred in any considerable quantity. Upon neutralizing the solutions on the two sides by carbonate of soda, it was found that an equivalent of sulphuric acid had travelled to the zincode. Upon reversing the arrangement, oxygen was collected as before from the zincode, and an equivalent of copper was thrown down upon the platinode, but no hydrogen was evolved.

(*z*.) The last experiments were varied by the substitution of solution of sulphate of potassa for the dilute sulphuric acid in combination with the sulphate of copper. When the copper solution was placed at the zincode, none of the metal passed over to the platinode, but a full equivalent of hydrogen was collected with alkali and acid at their respective electrodes. When the position of the two salts was reversed, the potassium travelled into the platinode cell, and was at once indicated by a precipitate of hydrated oxide of copper. The platinode plate was also covered partly with coherent copper, and partly with pulverulent metal, and only 3 cubic inches of hydrogen were collected for 71 cubic inches of mixed gases in the independent voltameter. None of the copper solution had penetrated to the zincode cell.

Thus it appeared that copper refused to exchange places with potassium in the circuit, as it had before refused to exchange with hydrogen, and so to pass from the zincode to the platinode.

(*a. a*.) *Sulphate of zinc* (ZnO, SO_3) was next subjected to the same treatment, and the results were exactly similar; the metal in all cases refusing like the copper to pass from the zincode division of the diaphragm cell to the platinode in any considerable quantity.

To ascertain whether the passage of the current from one electrolyte to another was in any way concerned in preventing the transfer of the base, we now resolved to employ *sulphate of copper* in solution *throughout* the whole arrangement, and having carefully ascertained the proportion of copper in solution, we placed 1500 grains of the liquid in each cell; metallic copper was thrown down on the platinode, and on precipitating the oxide from the liquid in the cell by potash, we found exactly the same amount of copper (taking the united quantities obtained from the oxide preci-

pitated, and from the metal deposited) as before the experiment. An equivalent of sulphuric acid was set free at the zincode, but the quantity of the copper solution in the cell continued the same as at the commencement. Copper thus appeared to refuse to exchange with itself in electrolysis.

Sulphate of zinc afforded results exactly similar.

(*a. b.*) That the diaphragm itself did not throw any obstruction in the way of such transfer we satisfied ourselves, by varying its substance, from membranes to porous earthenware; but this was put out of all doubt in the following manner. A long siphon tube reversed was filled with a strong solution of sulphate of copper, and two strips of copper were made the electrodes of the battery; the action proceeded very slowly, but after a long time the liquid in the platinode limb of the apparatus became sensibly lighter-coloured, while that in the zincode became darker; the oxysulphion disengaged at the latter point had dissolved the copper of the zincode, which, however, had no power to pass to the platinode, to replace the metal which had there been deposited.

The preceding experiments bear closely upon an observation familiar to persons engaged in electrotyping on the large scale, viz. that the solution around the platinode becomes impoverished, and at last nearly deprived of copper.

As it appears to be thus established, that in the electrolysis of complex electrolytes, the metals which are capable of decomposing water at ordinary temperatures, or whose oxides are largely soluble in water, are susceptible of transference in the voltaic circuit from the zincode to the platinode, whilst those which are not marked by this strong affinity for oxygen remain stationary; we were anxious to ascertain to which class ammonium belongs.

(*a. c.*) The apparatus was charged with a solution of *muriate of ammonia* (NH_4Cl) of known strength throughout; 35·5 cubic inches of hydrogen were collected from the platinode; the zincode liquid was yellow and smelt strongly of chlorine. By careful neutralization with muriatic acid, it was ascertained that an equivalent quantity of ammonia had been disengaged in the platinode cell, and by precipitation of the chlorine with nitrate of silver, from the liquid thus neutralized, we found that the solution contained the same amount of chlorine as before the experiment; the amount of ammonium in combination with it, must, therefore, have remained unchanged: it had received no addition by transfer from the zincode side. The results of the experiment were perfectly clear and decisive.

(*a. d.*) In an experiment which was made in the same manner with *microcosmic salt* (NaO, NH_4O, HO, P_2O_5), the sodium travelled to the platinode, but the whole of the ammonium remained in the zincode cell. Here a *polybasic* acid was used, and yet results similar to those with a monobasic acid obtained. We have still further evidence that the nature of the acid does not appear to be connected with this travelling of the base, from the fact, that when the double *tartrate of soda and ammonia*

$\left(\begin{matrix}NaO\\NH_4O\end{matrix}\right\}C_8\ H_4\ O_{10}\Big)$, was electrolysed, putting a solution of soda into the platinode cell, the sodium was found to have travelled, but ammonium had refused to do so, as in the other cases already mentioned.

It was thus ascertained, contrary to the anticipations which we had formed upon its extreme solubility, that ammonium is included in that class of basic compounds which refuse to travel in the voltaic circuit.

(*a. e.*) To show that a relation exists between the power of transference in the circuit, and the affinity of the oxides of the metals, for water, the results of three experiments may be taken with salts of potassa, baryta and magnesia. For one equivalent of force as measured by 71 cubic inches of mixed gases from the voltameter,

14·2 grains of potassium $=\frac{1}{8}$ equivalent were transferred from sulphate of potassa into sulphuric acid.

11·5 grains of barium $=\frac{1}{8}$ equivalent, were transferred from nitrate of baryta into a solution of the same salt.

1·0 grain of magnesium $=\frac{1}{12}$ equivalent, was transferred from sulphate of magnesia into sulphuric acid.

The experiments are not rigidly comparable together, nor must the quantities be taken as absolute determinations of the amount of each metal which travels in the circuit, but only as indicating a dependence of the transfer upon the attractive power of water or its elements.

The supposed anomalous transfer of sulphuric acid in the electrolysis of its mixture with water, the investigation of which cost so much labour upon a former occasion*, is now easily accounted for upon the hypothesis of the unequal transfer of the oxysulphion and hydrogen of the hydrate to their respective electrodes.

We were next induced to seek for some such connexion between the attraction of the different *acids* for water, and their transfer to the zincode. Our experiments had already embraced a great variety of acids, differing very much from one another in this respect, and in every case the transfer had taken place; but our attention had not yet been directed to the quantitative results.

(*a. f.*) As tungstic acid forms no definite hydrate and is insoluble in water, we selected it as an extreme test of the fact, and for this purpose prepared some pure *tungstate of soda* (NaO, WO_3) by fusing together equivalent quantities of the acid and carbonate of soda. The product of the operation was dissolved and crystallized. A solution was made which contained one-twentieth of its weight of the salt; it was placed in a diaphragm apparatus, and was found to conduct badly. The current was transmitted for $1\frac{3}{4}$ hour, when the zincode liquid was found to be distinctly acid, owing to the formation of a soluble bitungstate, and the platinode very strongly alkaline. Upon precipitating the tungstic acid from both sides, by hydro-sulphuret of

* Second Letter, p. 222.

ammonia and nitric acid, it was decidedly shown that a portion of the acid had travelled to the zincode cell.

Neutral *chromate of potassa* (KO, CrO_3), which contains an acid forming no definite hydrate with water, furnished a perfectly analogous result; and the same thing was observed in the experiments with *arsenite of potassa*.

(*a. g.*) The carbonic acid is one of those which seems to have the least affinity for water, but it has been already shown that in the electrolysis of the carbonates of potassa, soda and ammonia, it is given off as oxy-carbion at the zincode in equivalent proportions. We now repeated the experiment. The diaphragm cell was charged throughout with *carbonate of soda* (NaO, CO_2) of definite strength, and the gas tube from the zincode cell connected with a drying apparatus, and LIEBIG's bulbs. The amount of carbonic acid was ascertained by weighing the bulbs, and by careful precipitation of the liquid in the cell by caustic ammonia and chloride of barium. By these means it was ascertained that there had been a decided transfer of the acid to the zincode, though in much less proportion than that of the sodium to the platinode. From the quantities of acid transferred in these experiments (which quantities however, as they can be considered but approximations to accuracy, we have not thought it necessary to record), it would appear that those acids which form no definite hydrates, are transferred to the zincode in smaller quantity than is the case with those from which distinct hydrates are obtainable.

(*a. h.*) We were extremely anxious to devise some means of ascertaining the phenomena of transfer in the case of simple electrolysis, but were forced to abandon the attempt after many trials, from the difficulty of procuring any substance which would answer the purpose of a permeable diaphragm, whilst it could resist the heat which is necessary to bring the chlorides, or similar binary compounds into the liquid state. We, however, ascertained that when a solution of *chloride of sodium* in water was electrolysed, the chlorine was transferred to the zincode in greater quantity than the sodium from it.

(*a. i.*) To remove the possibility of its being thought that water in these experiments conveyed the force independently of the presence of the saline bodies (a supposition hardly reconcilable with the phenomena observed where the saline solution was used throughout the apparatus), the following experiments were made. The platinode cell of the diaphragm apparatus was charged with dilute sulphuric acid, and the zincode with distilled water; one diaphragm alone was employed. The arrangement conducted so badly, that in an hour and a half, with twenty cells of the battery, only 1·5 cubic inch of hydrogen was collected from the platinode. The apparatus was then recharged and the electrodes reversed, the water being now at the platinode, and the acid at the zincode. In an hour and a half 2·8 cubic inches of hydrogen were collected from the platinode. From the imperfect conducting power evinced by water in these and other experiments, we can hardly suppose that the current, in cases where the base is not transferred, is carried by the electro-

lysis of this fluid, mysterious and ill-understood as its electrical relations undoubtedly are.

7. In reviewing the results which we have obtained from the preceding experiments, and the conclusions which we are entitled to draw from them, it will, we think, be admitted that many of them are of the highest interest and importance, and some of them at variance with the fundamental principles of electrolysis which have been hitherto admitted.

We have seen that in every instance, the definite action of the electric current is maintained; and its passage through a compound liquid conductor is always marked by the disengagement at the platinode of hydrogen or the metallic element, or else of a group of substances, like ammonium, constituting an equivalent compound; and the simultaneous disengagement at the zincode of the non-metallic element, or a group of substances of iso-electric powers. Of such electrolytes it may be convenient to distinguish the following classes:—

1st. An electrolyte may consist of *simple ions*, and then must be constituted of a single equivalent of a metal (or H) for its cation, and a single equivalent of a non-metallic element for its anion; as K, I; Ag, Cl; &c.; they may be termed *simple electrolytes*.

2nd. An electrolyte may consist of a *compound cation*, a single equivalent of which must take the place of a metal; and a single equivalent of a *simple non-metallic anion*, as NH_4, Cl. Organic alkalies probably form compound cations of this nature, and when their salts are electrolysed, hydrogen is always disengaged with them at the platinode, as with ammonia; these and the following we may call *complex electrolytes*.

3rd. An electrolyte may consist of a *compound anion*, a single equivalent of which would take the place of the simple non-metallic anion, with a single equivalent of a *simple cation*, a metal (or H), as H, NC_2; K, SO_4; Na, NO_6.

4th. An electrolyte may consist of a single equivalent of a *compound cation*, and a single equivalent of *a compound anion*, as NH_4, SO_4.

These four cases may be included in the term *Monobasic Electrolytes*, as a single equivalent of force (measured by the voltameter) would electrolyse single equivalents of the electrolytes.

5th. An electrolyte may also consist of *two or more equivalents of a metallic cation* or (H), or of *single equivalents of two or more metallic cations* (or H); when the *anion* must consist of a *single equivalent of a compound ion*, as (K_2 $FeCy_3$). This compound ion, in the case of an oxysalt, contains the so-called anhydrous acid in combination with as many equivalents of oxygen as there are of metallic cations (or H) in the compounds, as (Na_3, $\overline{P_2 O_5}$, O_3).

In this case as many equivalents of force will be required for the electrolysis of one equivalent of the electrolyte as there are equivalents of metal (or H) in the cation. They may be denominated *Polybasic Electrolytes*.

In these compound anions and cations, it would appear that the oxygen which travels with the acid group, and the hydrogen which is evolved with the alkaline group, must be connected with the other elements whilst under the influence of the current in a manner differing from that in which the latter are combined together; for we have found that in most cases this connection is immediately dissolved upon their escape from the electric influence, whilst in some others their apparent permanent combination is only the effect of secondary action, where the oxygen is capable of forming a chemical compound of a higher degree of oxygenation, and like other secondary actions of a similar nature, is variable in its amount.

8. The disengagement of the cation and anion of an electrolyte in equivalent proportions is not always effected, as is commonly represented, by their simultaneous transfer in opposite directions to their respective electrodes, in the exact proportion of half an equivalent of each; but is sometimes brought about by the transfer of a whole equivalent of the anion to the zincode, whereby a whole equivalent of the cation is left uncombined at the platinode; or by transfer of unequivalent portions of each in opposite directions, making however together a whole equivalent of matter transferred to one electrode or the other; or speaking more correctly, *by the transfer of a quantity of matter capable of exerting one equivalent of chemical force*, so that when the anion *transferred* to the zincode exceeds half an equivalent, the cation transferred to the platinode is in an equal proportion less than half an equivalent, and *vice versâ*; the anion and cation *set free* being always in equivalent proportions. We have, however, in no case observed the transfer of a whole equivalent of the cation to the exclusion of the anion.

These facts are, we believe, irreconcilable with any of the molecular hypotheses which have hitherto been imagined to account for the phenomena of electrolysis, nor have we anything more satisfactory at present to substitute for them; we shall therefore prefer leaving them to the elucidation of further investigation, to adding one more to the already too numerous list of hasty generalizations.

II. *On the Thermal Changes accompanying Basic Substitutions.* By THOMAS ANDREWS, *M.D., M.R.I.A., Professor of Chemistry in the Royal Belfast Institution. Communicated by* MICHAEL FARADAY, *D.C.L., F.R.S., &c. &c. &c.*

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IN a communication made to the Royal Irish Academy, nearly three years ago, I described a series of experiments on the heat evolved during the mutual reaction of acids and bases upon one another, from which the general conclusion was deduced, that when the influence of all extraneous circumstances is eliminated, the heat is determined by the basic and not by the acid element of the combination. Nearly at the same time an important memoir was published by M. HESS on thermo-chemistry, in which an opposite result was arrived at, deduced however from a very limited number of experiments, and merely announced by its author, as a probable generalization, the accuracy of which could only be determined by further researches. The principle, as stated by M. HESS, is this, that different bases disengage the same quantity of heat in combining with the same acid*.

In the present state of chemical knowledge we cannot attempt the resolution of this problem by direct experiments on the anhydrous acids and bases, even if we adopt the hypothesis, no longer universally admitted by chemists, that the proximate constituents of neutral salts are the ordinary acids and bases. Experiments performed with the concentrated acids are not adapted to yield simple results, since the mere circumstance of dilution with water produces the evolution of large quantities of heat in the case of some acids, and none, or a very slight variation of temperature in the case of others. It is for this reason that when an alkaline solution is neutralized by the addition of an equivalent of nitric acid, the heat disengaged is very different, according to the state of concentration of the acid; while the same circumstance produces little or no effect, when the tartaric acid is employed. If we institute a further comparison between the results, it will be found that while no simple relation exists between the temperatures obtained with different acids in a concentrated state, there is a very close approximation to an equal development of heat when the same base is neutralized by any dilute acid.

In many apparently simple reactions it is difficult to ascertain with certainty all the combinations and decompositions which occur, and our thermal results become proportionally difficult to interpret. Even to deduce the heat due to the combination of an anhydrous acid and alkali from that evolved when their solutions are

* POGGENDORFF's Annalen, Bd. lii. 107, or Phil. Mag. v. xx. p. 1.

mixed together, is a question of very great difficulty, requiring the previous determination of many data, all of which are in few instances capable of being discovered by experiment. The liquids before mixture are, in fact, solutions of the acid and alkali in the state of hydrates, and as large quantities of heat were evolved during the formation of these hydrates, and generally also during their subsequent solution, an equal absorption of heat will take place when these combinations are destroyed. A further allowance is also required for the effect of the solution of the resulting compound. After making all these corrections it is doubtful whether the result finally obtained would not be a theoretical or imaginary number.

If we adopt the view, now generally admitted by chemists, that the hydrated acids are in reality compounds of the pure acids with water performing the functions of a base, the heat produced when a dilute acid is neutralized by a base will arise from the latter displacing an equivalent of basic water*, and the general result, before referred to, may be thus expressed. "When the same base displaces water from any of its acid combinations, the heat disengaged is nearly the same." If for basic water we substitute any base, the law will receive a very general form as follows:—

When one base displaces another from any of its neutral combinations, the heat evolved or abstracted is always the same, whatever the acid element may be, provided the bases are the same.

The following experiments were undertaken for the purpose of determining the accuracy of this principle. The base selected to displace others was the hydrate of potash, and it was always employed in a state of dilute solution. The strength of the solution was ascertained by neutralizing a determinate quantity with sulphuric acid of known strength. The required quantity was weighed in a thin brass vessel of a long cylindrical form, coated externally with copal varnish. The latter precaution effectually protected it from the action of all metallic solutions. The equivalent solution of the salt to be decomposed was contained in a thin glass jar, supported within a larger one, by means of a projecting rim. The whole was so adjusted that when the brass vessel with its contents was cautiously placed in the saline liquid it was sufficiently buoyant to float, and, at the same time, it extended through nearly the entire depth of the liquid. The weight of the two liquids taken together was 1000 grains, of which the saline solution formed about 700 grains. To bring the two liquids to the same temperature, a rapid rotatory motion was given to the inner vessel, by moving a light glass stirrer round in it. In the outer vessel a very delicate thermometer with a long cylindrical bulb was suspended. As soon as a perfect equilibrium of temperature was established between the two fluids, the position of the thermometer was carefully observed. The edge of the brass vessel was then grasped with pincers, and its contents quickly added to the saline solution. The mixture was now rapidly stirred and the new position of the thermometer noted. The brass vessel was not again introduced into the liquid after the mixture had taken place.

* Transactions of the Royal Irish Academy, v. xix. 247.

The heat evolved, except in a few instances, did not exceed 3°; and it was so arranged that the final temperature of the liquid was from 0°·3 to 1° higher than that of the surrounding air, according to the total amount of heat. When a diminution of temperature occurred the adjustments were accordingly modified.

To this method of operating several objections will at once occur, but numerous trials have satisfied me that it gives very accurate results when the variations of temperature are not considerable. The important condition of bringing the two liquids precisely to the same temperature in a short space of time is completely attained. The principal source of error is the heating or cooling of the alkaline solution during the moment of being transferred into the outer vessel, and, if the difference between the initial temperature of the fluid and that of the air had been considerable, this would have been a serious objection to the process. The difference in question rarely exceeded 2°. As a few drops of the alkaline solution remained adhering to the interior of the vessel, an excess of 3 grains was taken, which I found to be an exact allowance for the loss. A similar portion of the saline solution adhered to the outer surface of the brass vessel, but as both liquid and salt were carried off together, the error from this cause did not in any instance amount to more than a fraction of a hundredth of a degree. The exposure to the air of the caustic solution during the few minutes occupied in equalizing the temperatures induced no sensible error.

The strength of the solution was such, that when a sulphate was employed, the entire fluid after mixture contained one per cent. of anhydrous sulphuric acid. Hence the required quantity of any salt was obtained by dividing its atomic weight by the atomic weight of sulphuric acid. The alkaline liquid contained from $\frac{1}{100}$th to $\frac{1}{100}$th of potash more than was sufficient to decompose the salt.

The thermal value in water of the bulb of the thermometer employed was 6 grains; that of the glass vessel and stirrer (the specific heat of the glass being 0·140) 68 grains; making the entire value of the vessels 74 grains. The brass vessel being removed altogether after the temperatures were adjusted is of course not included. The corresponding value of the vessels in terms of the liquid obtained is 76 grains. The temperatures found are therefore corrected for the vessels by multiplying them by 1·076.

Finally, a further correction is required for the specific heats of the solutions and precipitates obtained. But as the accurate determination of the specific heat of any substance requires great care and much time, I did not attempt to examine separately the specific heat of the product of every operation. I determined, however, very carefully the specific heats of the four principal solutions formed, and estimated the specific heats of the precipitated oxides (their weights taken in the anhydrous state) from the experiments of M. Regnault. The liquids examined were solutions (of the normal strength) of the sulphate, nitrate, and acetate of potash, and of the chloride of potassium, and their specific heats were found to be respectively 0·973, 0·975, 0·971 and 0·971*.

* See Note at the end.

I have collected the experimental results into separate tables. The first column of each table contains the name of the salt which was decomposed; the second, its weight; the third, the change of temperature found by experiment; the fourth, the same corrected for the vessels or referred to 1000 parts of the resulting mixture; and the fifth, the same referred to 1000 parts of water.

Salts of Lime.

Salt.	Weight.	Found.	Ref. to liquid.	Ref. to water.
$CaO.NO_5$	20·6	−0°·34	−0°·37	−0°·36
$CaO.NO_5$	20·6	−0·32	−0·35	−0·34
$CaO.S_2O_3.6HO$	32·7	−0·35	−0·38	−0·37
$CaO.S_2O_3.6HO$	32·7	−0·31	−0·34	−0·33
CaCl	13·9	−0·34	−0·37	−0·36
CaCl	13·9	−0·36	−0·39	−0·38
$CaO.\overline{A}.Aq$	22·2	−0·35	−0·38	−0·37
$CaO.\overline{A}.Aq$	22·2	−0·35	−0·38	−0·37

The nitrate was cautiously dried on a sand-bath; in one experiment the solution was neutral; in the other, it had a slight alkaline reaction. The chloride was dried at a low red heat, but not fused. Its solution was distinctly alkaline, as this salt undergoes slight decomposition from the gentlest ignition. Of the acetate, dried in a warm atmosphere, 22·64 grains yielded 12·70 grains carbonate of lime, from which the required quantity, as given in the table, was calculated.

The negative sign indicates that when potash displaces the base in these salts, a diminution of temperature takes place. The accordance of the results within the limits of the errors of experiment is perfect.

Salts of Magnesia.

The salts of magnesia are very imperfectly precipitated in the cold by caustic potash, and therefore the change of temperature indicated by the thermometer is only a part of that produced by the substitution of potash for magnesia. A depression of temperature occurred with these salts as with the preceding, amounting to between 0°·10 and 0°·15, in experiments made with the sulphate and chloride and an equivalent of potash. With a larger proportion of the latter, a greater depression of temperature occurred, but the substitution appeared to be still incomplete.

Salts of Barytes and Strontia.

In numerous experiments with the nitrates of barytes and strontia, and with the chlorides of barium and strontium, no change of temperature occurred. The solutions were taken so dilute that a mere cloud appeared on mixture, consisting chiefly of a trace of carbonate. It is true that we have no positive proof that decomposition occurs unless stronger solutions are employed and a precipitate formed, but the comparative insolubility of these bases renders it very probable that in all cases substitution does take place.

Salts of Soda.

Salt.	Weight.	Found.
$NaO.NO_5$	21·4	+0°·14
$NaO.NO_5$	21·4	+0·13
$NaO.SO_3.10HO$	40·3	+0·06
$NaO.SO_3.10HO$	40·3	+0·07
Na Cl	14·6	+0·04
Na Cl	14·6	+0·05
$NaO.CO_2.10HO$	35·8	+0·07
$NaO.CO_2.10HO$	35·8	+0·05

Salts of Ammonia.

Salt.	Weight.	Found.	Ref. to liquid.	Ref. to water.
$AdH_3O.SO_3.HO$	18·74	+0°·70	+0°·75	+0·73
$AdH_3O.NO_5$	19·98	+0·69	+0·74	+0·72
$AdH_3.Cl$	13·33	+0·70	+0·75	+0·73
$AdH_3O.C_2O_3.HO$	17·72	+0·70	+0·75	+0·73
$AdH_3O.C_4H_3O_3.HO$	25·24	+0·69	+0·74	+0·72

These experiments repeated with another thermometer gave the following results, all corrections being made:—sulphate, 0°·76; nitrate, 0°·77; muriate, 0°·76; oxalate, 0°·75, and tartrate, 0°·76. These numbers agree perfectly with one another, but their average is 0°·03 higher than the above. Before examining the thermal relations of these salts, it is necessary to ascertain that their solutions are quite neutral, as the slightest excess of acid would altogether derange the results.

I attempted to prepare a solution of the hydrocyanate of ammonia, by mixing together solutions containing an equivalent of hydrocyanic acid and an equivalent of ammonia. On decomposing this liquid by potash, an elevation of temperature occurred in different trials of 0°·87 and 0°·90, which approximates to the preceding results. The anomalies presented by the hydrocyanic acid in combining with the alkalies render this fact of some importance.

The so-called neutral phosphate and arseniate of ammonia are salts anomalous in composition, and on theoretical grounds ought to differ in thermal properties from the other ammoniacal salts. If a second equivalent of ammonia (in dilute solution) be added to a solution of the ordinary neutral salts of ammonia, no change of temperature occurs; but the same addition to the neutral phosphate produced an elevation of temperature of 0°·18. The latter salt, however, loses a part of its ammonia during evaporation with so much facility, preserving always its alkaline reaction, that I am not sure whether this is a property of the salt when of normal composition, or arose from its having lost a portion of its base before solution. When the same salt was decomposed by potash, the results were not uniform; in one experiment the heat amounted to 0°·98; in another, made with the same salt, after exposure for a very short time to a warm dry atmosphere, the heat was 1°·60; and in a third, performed

with a solution of the latter previously saturated with ammonia, the thermometer rose 1°·00. If we assume the heat produced during the decomposition of potash to be 0°·99, and subtract from this 0°·18, we shall have for the heat produced by the substitution of potash for ammonia 0°·81, which is nearly the same result as before. The thermal properties of all the alkaline phosphates and arseniates are very complicated, and will require further investigation.

Salts of Manganese.

Salt.	Weight.	Found.	Ref. to liquid.	Ref. to water.
$MnO.SO_3$	18·9	$+\mathring{1}\cdot00$	$+\mathring{1}\cdot08$	$+\mathring{1}\cdot04$
$MnO.SO_3$	18·9	+1·00	+1·08	+1·04
MnCl.Aq	24·9	+1·00	+1·08	+1·04
MnCl.Aq	24·9	+1·01	+1·09	+1·05
$MnO.\bar{S}.Aq$	30·7	+1·11	+1·19	+1·15

The composition of the chloride and succinate was determined by converting them into sulphates. 17·05 grains of the chloride gave 12·94 grains of sulphate, and 11·24 grains of succinate gave 6·91 grains of the same, from which the above quantities were calculated. The succinate, it will be observed, produces a little more heat than the other salts. It is probable indeed that all these numbers are rather above the truth from the rapidity with which the precipitate absorbs oxygen. This produces a slight but distinct evolution of heat for some minutes after the precipitation takes place.

Proto-salts of Iron.

Salt.	Weight.	Found.	Ref. to fluid.	Ref. to water.
$FeO.SO_3.7HO$	34·5	$+\mathring{1}\cdot52$	$+\mathring{1}\cdot64$	$+\mathring{1}\cdot58$
FeCl . 4HO	24·6	+1·57	+1·69	+1·63
FeCl . 4HO	24·6	+1·53	+1·65	+1·59

The same observation applies to these results as to the preceding.

Salts of Zinc.

Salt.	Weight.	Found.	Ref. to liquid.	Ref. to water.
$ZnO.SO_3$	20·06	$+\mathring{1}\cdot73$	$+\mathring{1}\cdot86$	$+\mathring{1}\cdot79$
$ZnO.SO_3$	20·06	+1·76	+1·89	+1·82
$ZnO.NO_5.Aq.$	29·56	+1·68	+1·81	+1·74
$ZnO.NO_5.Aq.$	29·56	+1·65	+1·78	+1·71
$ZnO.NO_5.Aq.$	29·56	+1·69	+1·82	+1·76
ZnCl	16·87	+1·65	+1·78	+1·71
ZnCl	16·87	+1·68	+1·81	+1·74
ZnCl	16·87	+1·67	+1·80	+1·73
ZnBr	27·57	+1·65	+1·78	+1·71
ZnI	39·54	+1·68	+1·81	+1·74

The sulphate was rendered anhydrous by cautious ignition. The nitrate was evaporated till it became a solid mass on cooling. 20·17 grains of the hydrated salt left 6·85 grains of the oxide on ignition. The chloride was cautiously fused and weighed in a covered crucible. The bromide and iodide were dried on a hot sand-bath, but not fused. The three latter compounds are slightly decomposed by the heat required to deprive them of all moisture. Hence the increments of heat obtained with them must be a little below the truth. All the above salts of zinc were precipitated by an exact equivalent of potash, and the precipitate thus formed was found to consist of the hydrated oxide. But when the acetate of zinc is treated in the same manner, the precipitate which falls is a subsalt. The supernatant liquid still contains a portion of the salt of zinc, and the addition of more potash produces a further precipitate. For this reason, on precipitating an equivalent of this salt by an equivalent of potash, the thermometer rose only 1°·31. On attempting to effect a more complete decomposition by using a double equivalent of potash, the heat obtained was rather less; but it is doubtful whether the additional quantity of alkali effected a more perfect substitution, while the precipitate was, at the same time, to a great extent redissolved. This is an interesting example of an apparent exception to the law of equibasic heat arising from a corresponding anomaly in the chemical reaction.

Salts of Mercury.

The only salt of mercury adapted to these inquiries is the chloride. Half the usual equivalent of it (17·1 grains) and of the potash solution gave, in three experiments, 0°·90, 0°·86 and 0°·89, which, all corrections made and the final results doubled, correspond to 1°·89, 1°·81 and 1°·87. I have not been able to confirm this result by precipitating the oxide from any other salt. The bromide has too little solubility in cold water. The cyanuret is not decomposed by potash, and accordingly, no heat is produced when their solutions are mixed. That the potash has not decomposed the salt is further proved by the circumstance, that on neutralizing it with an acid, the same increment of temperature occurred as if the alkali had been in a free state. The sulphate and nitrate are both decomposed when their solutions are diluted. It has indeed been lately asserted that a solution of the neutral nitrate may be obtained by precipitating the chloride with nitrate of silver. This is a mistake, as the usual decomposition occurs in this case. In fact, the solution of the supposed neutral nitrate, instead of the acid reaction of the chloride from which it is formed, intensely reddens litmus paper. If a similar experiment be made with other metallic chlorides, capable of forming neutral nitrates, no perceptible change of reaction will be found to occur. These observations fully explain the anomalies which I formerly pointed out in the action of the dilute acids on the red oxide of mercury.

Salts of Lead.

Salt.	Weight.	Found.	Ref. to liquid.	Ref. to water.
$PbO.NO_5$	41·34	+2·77	+2·98	+2·83
$PbO.NO_5$	41·34	+2·77	+2·98	+2·83
$\frac{1}{2}(PbO.NO_5)$	20·67	+1·39	+1·49	+2·90
$\frac{1}{2}(PbO.NO_5)$	20·67	+1·37	+1·47	+2·86
$\frac{1}{2}(PbO.\bar{A}.3HO)$	23·64	+1·32	+1·42	+2·77
$\frac{1}{2}(PbO.\bar{A}.3HO)$	23·64	+1·33	+1·43	+2·80

In the last four experiments half quantities were taken, but the results are all reduced to the common standard in the fifth column. After the precipitate had subsided, the clear solution above was found to be highly alkaline, capable of precipitating freely the salts of lead, and containing at the same time a small quantity of lead in solution. These facts are well known, and prove that the preceding numbers represent only a part of the heat due to the substitution of potash for the oxide of lead. Their accordance shows that the salts of lead, when similarly treated with caustic potash, give equal quantities of heat.

Salts of Copper.

Salt.	Weight.	Found.	Ref. to liquid.	Ref. to water.
$CuO.SO_3$	19·90	+2·86	+3·08	+2·97
$CuO.SO_3$	19·90	+2·86	+3·08	+2·97
$CuO.NO_5.Aq$	30·53	+2·86	+3·08	+2·97
$CuO.NO_5.Aq$	30·53	+2·86	+3·08	+2·97
$CuCl$	16·72	+2·81	+3·02	+2·91
$CuCl$	16·72	+2·84	+3·05	+2·94
$CuCl$	16·72	+2·80	+3·01	+2·90
$CuO.\bar{A}.HO$	24·87	+3·08	+3·30	+3·18
$CuO.\bar{A}.HO$	24·87	+3·02	+3·25	+3·12
$CuO.\bar{A}.HO$	24·87	+3·06	+3·29	+3·16

The sulphate and chloride were weighed in the anhydrous state. The nitrate was taken in the state of moist crystals, and their composition determined by calcination, 8·73 grains yielding 2·83 grains oxide by calcination. The result with the acetate showing a small excess of heat, I endeavoured to discover whether it could be referred to some peculiarity in the precipitate, or in the composition of the salt. The precipitate obtained in the first experiment was collected and found to weigh 10·01 grains, or 1 per cent. more than the theoretical quantity, which, supposing an equal excess of caustic potash to have been present, could only have produced an error of 0°·03. Of the crystals employed in the last experiment, 9·40 grains being digested with nitric acid and afterwards calcined, yielded 3·74 grains oxide, which is exactly the theoretical result. It appears, therefore, that the acetate of copper, when decomposed by potash, produces about $\frac{1}{11}$th more heat than the other salts of copper.

Salts of Silver.

The nitrate is the only salt of silver I have examined, and the experiment was performed in order to ascertain the position of the oxide of silver as a thermal base. The full equivalent 42·48 grains decomposed by potash, gave 3°·88, or referred to the resulting liquid 4°·17, or to water 3°·95. Two similar experiments with half an equivalent gave nearly similar results, viz. 3°·90 and 3°·94, all corrections being made and the final results doubled to bring them to the ordinary standard.

Sesquisalts of Iron.

The bases hitherto examined being all of the form MO, it was of importance to determine how far the same principle would apply to bases of the form M_2O_3. The sesquisalts of iron appeared to be the best adapted for experiment, but it is difficult to procure them in a neutral state. The most certain method of effecting this object, is to pass a current of chlorine gas to saturation through solutions of the protosalts, expelling afterwards the excess of chlorine by heat. In this way a solution of sesquichloride may be easily procured from the protochloride, and a mixture of sesquisulphate and sesquichloride from the protosulphate. But as the resulting sesquicompounds require one half more potash for decomposition than the protocompounds from which they are derived, it was necessary, in order to preserve the usual quantity of potash, to take only two-thirds of an equivalent of the latter. Accordingly 16·40 crystallized protochloride of iron, converted into sesquichloride and decomposed by potash, gave, in different experiments, 3°·83, 3°·75 and 3°·74, which, all corrections made, correspond to 3°·97, 3°·89 and 3°·88. Of the crystallized protosulphate, 23·00 grains, treated in the same way, gave 4°·09, 4°·11 and 4°·12, corresponding to 4°·25, 4°·27 and 4°·28. These results, although not identical, present a sufficiently close approximation, particularly when the uncertainty of the original composition of the crystallized salts, and the difficulty of expelling without decomposition all the excess of chlorine, are considered. Another circumstance, whose influence it is difficult to appreciate, but which will tend to modify these results, is this, that the precipitate obtained always contains potash united by so strong an affinity to the hydrated sesquioxide that the action even of hot water produces only a partial separation. It is very probable that this may occur to a different extent with different salts, and hence may be one source of variation in the thermal effects.

On reviewing the foregoing results it will be observed, that while the effect of the substitution of potash for different bases produces thermal changes, varying from −0°·34 to +4°·28, the greatest uniformity prevails in those obtained with the salts of each separate base. It is true that in some instances slight differences do manifest themselves, but these differences, I apprehend, are in general not greater than occur in the chemical reactions. It is of course essential to a perfect uniformity of result, that exact equivalents of the salt and base should be employed, and that a complete

substitution should take place. But these conditions can rarely be fulfilled. It is important, however, to remark, that, with one or two exceptions, the observed deviations are in the same direction which theory would indicate. The difficulty of obtaining most of the metallic salts in a perfectly neutral condition, and in a definite state of composition, is well known; and in the case of deliquescent compounds, a separate analysis of the specimen can rarely be employed with advantage. The variable nature of the precipitate arising from imperfect substitutions is a fertile source of divergences in the results, and the tendency to this is further increased by the necessity of performing all the experiments without the application of external heat. The formation of a subsalt produces less heat than the precipitation of the hydrated oxide, for the obvious reason that in the former case an imperfect substitution takes place. A remarkable example of this has been already cited in the action of potash on the acetate of zinc, where a great deviation from the usual development of heat is distinctly shown to depend upon the precipitate being a subsalt. The same cause, no doubt, frequently interferes with the accuracy of the result in other cases, where only a small portion of subsalt is formed. In other examples, part of the original base still remains in solution; and in others again, portions of the substituting base are carried down along with the precipitate. When we take into consideration all these sources of error, the numerous instances of perfect agreement with, as contrasted with the few examples of slight deviation from, the general law of the heat of substitution being equal for the same bases, appear to be sufficient fully to establish its accuracy.

It may be here observed that the accuracy of this principle will not be in any way affected whatever views may be adopted, as to the exact changes which occur when one base displaces another. Whether we consider the final result to arise from the simple substitution of one base into the position occupied by another, or from a series of distinct chemical changes, each producing a certain thermal effect, the general facts now established will not be the less rigorously true.

The separation of most of the bases in a solid form, will of course tend to produce heat, and as this will vary with different precipitates, the numbers for the insoluble bases cannot be exactly compared with one another. The amount of the latent heat due to precipitation is unknown, but it must be the same whenever the same precipitate is formed. The correction for this cause will, therefore, be a constant quantity for the salts of the same base, and if applied, could not affect the equality of the foregoing groups of numbers. It is important to observe, that, notwithstanding the heat due to the formation of the precipitates, a diminution of temperature occurs when potash is substituted for lime or magnesia.

On a first view this last fact appears to prove that potash is a less powerful thermal base than lime or magnesia, but a closer examination will show that it is at least premature to draw such a conclusion. It must be remembered that we are imperfectly acquainted with all the chemical changes which accompany the substitutions

under consideration. We know that the substituting base existed in the state of a hydrate before mixture, and that after mixture the displaced base is also obtained in the same state. But we have no means of discovering with certainty in what state these bases exist in the solutions of their neutral combinations. If we assume that they exist in the state of hydrates, then the numbers given before will express exactly the heat arising from the chemical substitutions. But if we suppose that the potash separates from its combination with water, and the lime on the other hand unites with water during the course of the experiments, then these numbers will be the general result of a series of complicated changes. Other suppositions may be made, but we cannot prove the truth of any of them. One thing is certain, that whatever these unknown changes may be, they will be precisely similar when the bases employed are the same. Hence the foregoing experiments are sufficient to prove that with the same bases, the heat arising from basic substitutions is always the same, although the numbers may not express the entire change of temperature due to that cause.

Among the circumstances which may perhaps be supposed to influence these results, are the changes of temperature arising from the solution of the saline compounds in water,—a subject recently investigated by Mr. GRAHAM. But although it is true that a different salt remains in solution after substitution from that which was present before, yet it must be observed, that neither salt during the process assumes the solid state, and the changes of temperature in question are essentially dependent on that condition. For this reason, it appears to me that the thermal effects arising from solution are not in any way brought into action in the course of these experiments.

The same general principle will be found to include nearly all the thermal results I formerly described, as arising from the action of bases and dilute acids upon one another, and upon solutions of neutral salts. In cases where the same base (as before mentioned) displaced water from any of its combinations with the acids, the heat evolved was nearly (but not exactly) the same. On the contrary, where no basic substitution occurred, there was either none, or a very slight variation of temperature. As examples of the latter, I may refer to the absence of any variation of temperature when solutions of a neutral salt and hydrated acid, capable of combining to form an acid or double salt, are mixed. Mr. GRAHAM has indeed lately made the observation, that the formation of certain acid sulphates is attended with a diminution of temperature, but the change of temperature so produced is of small amount compared with that arising from basic substitutions. It is difficult to prove that combination actually takes place when solutions containing the proximate constituents of an acid or double salt are mixed. But, as far as I have investigated the subject, the thermal properties of the solutions thus formed are identical with those of solutions prepared by dissolving the crystallized acid or double salt in water. Thus, if we prepare solutions of crystallized binoxalate and quadroxalate of potash, and add to them exactly the

quantity of potash required for neutralization, the usual heat due to the substitution of potash for water will be obtained.

I have formerly shown that there is a definite evolution of heat when solutions of the common alkaline phosphates and arseniates are mixed with a solution containing an additional equivalent of base, while no change of temperature occurs when a solution of the pyrophosphate of soda is similarly treated. In the former case, it has been shown by Mr. GRAHAM that an atom of basic water is displaced by an atom of alkali; in the latter case, no basic water is present.

In the preceding observations it has been assumed, that if the union of two substances be attended with the evolution of a certain definite quantity of heat, their separation will be attended with the absorption of the same quantity of heat. Although this proposition in the abstract is very probable, it requires to be demonstrated by direct experiment, and it is the more important to do so, as it will furnish, if true, a means of verifying the accuracy of our results. The reactions now described enable us to test it by experiment in one particular set of cases. In fact, if we take three bases, such as potash, oxide of copper, and water, capable of displacing one another in the above order, and if we measure the changes of temperature produced when the first and second, first and third, and second and third bases displace one another, then the change of temperature arising from the first substitution should be equal to the difference between the changes of temperature produced by the two latter. A few examples will illustrate this point.

The numbers expressing the heat developed when the nitrate of water is decomposed by potash and lime are 6°·76 and 7°·20. The difference of these numbers is −0°·44, indicating that a depression of temperature to that amount ought to take place when the former base is substituted for the latter. We have before seen that the result of the direct experiment is −0°·37. In this and the following cases, the temperatures corrected only for the vessels are adopted, because I have not determined the specific heats of the metallic solutions. The error in the comparison from this circumstance is wholly insignificant.

The heat produced in two experiments in which sulphate of water was decomposed by potash was 7°·24 and 7°·22. The same compound decomposed by ammonia gave in different trials 6°·40, 6°·53 and 6°·51. The difference of the means of these numbers is +0°·74. The direct experiment gave in one experiment +0°·75, in another +0°·78.

The corresponding number which expresses the substitution of oxide of zinc for water in the sulphate of water is 5°·40, and this taken from 7°·22 leaves 1°·82 for the heat due to the displacement of oxide of zinc by potash. The direct experiment gave 1°·87.

Two experiments were made to determine the heat arising from the substitution of oxide of copper for the base in the nitrate of water. In one of these experiments the hydrated oxide was taken; in the other, the anhydrous oxide, obtained by precipi-

tating a hot solution of the sulphate of copper by caustic potash. The results agreed closely with one another, being 3°·52 and 3°·53. Taking the mean of these numbers from 6°·76, we have 3°·23 to express the heat due to the substitution of potash for oxide of copper. The result of the direct experiment was 3°·08.

A similar comparison cannot be made with the salts of magnesia or lead, because an imperfect substitution takes place when their solutions are precipitated by potash.

If we compare in like manner the other results contained in the paper before referred to, it will be found that the differences between theory and experiment rarely exceed 0°·3,—a close approximation when the defective method of investigation formerly employed, and the great difficulty of obtaining accurate results with the insoluble bases are considered.

It may be remarked that there is no notable difference in the heat developed during the solution of the oxides of zinc and copper in the hydrous and anhydrous states, which makes it probable that the heat due to the combination of those bases with water is not considerable.

The preceding experiments appear to me to be sufficient to establish the accuracy of the general principle already stated, that when one base displaces another from any of its neutral combinations (all being taken in the state of dilute solution) the heat is always the same with the same bases, but in general different with different bases. The small deviations from this law in the case of the ordinary bases are not greater than we observe in other investigations connected with heat; and I have before pointed out many circumstances which tend to account for some of these deviations. The results obtained during the decomposition of the salts of water present more remarkable anomalies, as I have formerly shown. Of these, the greater development of heat during the neutralization of the dilute sulphuric acid by alkaline solutions deserves particular notice, and still remains unexplained. The anomalies presented by the oxide of mercury and hydrocyanic acid, I have partly traced to their source. But the other results approximate too closely to one another to leave any doubt that the same principle applies to the decomposition of the salts of water as well as to that of the salts of other bases.

I have not succeeded in connecting the thermal developments, as given by experiment, with any other property of the bases. In the following list I have arranged the bases hitherto examined in the order of the thermal results, attaching to each the number expressing the change of temperature produced when its salts are decomposed by potash.

CaO	−0°·36	ZnO	+1°·74
BaO	0·00	HgO	+1·86
SrO	0·00	PbO	+2·82+
NaO	+0·08	CuO	+3·00
AdH_2O	+0·74	AgO	+3·93
MnO	+1·07	Fe_2O	+4·09
FeO	+1·60		

Supplementary Note on the Determination of the Specific Heats of Fluids.

The accurate determination of the specific heats of fluids is of so much importance in all inquiries connected with the heat of combination, that I have taken some pains to introduce greater simplicity and accuracy into the methods hitherto employed for that purpose. The process I am about to describe is a modification of that adopted by M. Regnault in his valuable researches on the specific heats of simple and compound bodies, and I am also indebted to the same accurate philosopher for a knowledge of the most important precautions to be taken in inquiries of this kind.

The general principle of the following method is to compare the increments of temperature produced by the cooling of a hot body in water and in the fluid under examination. But instead of taking, as is usually done, a ball of heated metal, whose temperature at the moment of immersion cannot be known with absolute precision, I employed a thermometer with a very large reservoir, and so adjusted that the mercury does not appear in the stem till it is heated to nearly the boiling point of water. The cylindrical reservoir is about two inches long, and half an inch in diameter. A mark is placed on the stem corresponding to 201° Fahr., which point is situated about an inch and a half from the reservoir. This instrument is easily heated by means of a very simple apparatus till the mercury rises a little above the mark.

The first step of the process is to determine accurately the thermal value of the reservoir with a small portion of the stem adjacent to it in terms of water. For this purpose, a certain weight of water is placed in a cylindrical vessel of thin brass, which is suspended within a larger vessel of tin plate. A very delicate thermometer, with a long cylindrical bulb (capable of being read with ease to $\frac{1}{50}$th part of a degree), is suspended in the water, and the whole is so arranged that the initial temperature of the fluid is about 5° below that of the surrounding air.

The observer, previously agitating with a very light glass stirrer the water in the brass vessel, reads the temperature to an assistant, who notes it down and also marks the time. The former then removes the large thermometer from the heating apparatus (the disturbing influence of which is carefully prevented by a wooden screen) and, holding it at a suitable distance from the water, watches the descent of the mercury till it reaches the mark, when he instantly immerses it. The time of immersion is again noted, and the whole is gently agitated for $3\frac{1}{2}$ minutes in the fluid. The temperature of the latter having now always attained a maximum, the new position of the thermometer is observed. The final temperature is never allowed to be more than 2° higher than the air.

The corrections for the heating and cooling influence of the air are very small when all the above conditions are fulfilled. They must not, however, be neglected. The rate of heating for each degree of depression per minute was found to be 0°·01, and as from 12 to 20 seconds usually elapsed between the observation of the initial temperature and the immersion of the heated instrument, the correction for that period of the observation was easily made. It was assumed that during the minute subsequent

to the immersion, the heating and cooling processes counterbalanced one another; and the correction for the last $2\frac{1}{2}$ minutes was made on the hypothesis that the fluid during that period was at the final maximum. The rate of cooling was found to be about 0°·012 per minute, for each degree of excess, the fluid being kept in constant agitation.

Knowing the weight of the water, the value in terms of water of the different parts of the apparatus, the temperature gained by the water and lost by the instrument, we possess all the data necessary to calculate the thermal value of the latter in terms of water.

By repeating the same experiment with an equal bulk of the liquid whose specific heat is required, we obtain the thermal value of the same instrument in terms of the liquid. From these values the specific heat may be calculated. An equal bulk of the liquid is employed in order to have the instrument immersed in all cases to precisely the same depth, and, for a similar reason, it ought to be always introduced in a perpendicular direction into the fluid and maintained in the same position during the agitation. Before calculating the final result, it is necessary to obtain an approximate one, in order to find the thermal value of the brass vessel, &c. in terms of the liquid. In actual practice this is easily effected without involving any sensible error. If the specific heat of the liquid differ considerably from that of water, the correction for the heating and cooling influence of the air must also be modified.

The weights of the different parts of the apparatus and their value in water are as follows:—

Mercury in bulb of thermometer by which the increment of temperature was measured 300 gr. × 0·033	9·9
Glass in bulb and immersed portion of stem 24 gr. × 0·14 . . .	3·3
Glass stirrer 20 gr. × 0·14	2·8
Brass vessel 420 gr. × 0·094	39·5
Value of entire apparatus	55·5

The value of the apparatus in terms of the following solutions is 57·0 grains.

If we now make

D. The difference between 201° and the final temperature of the liquid, or the heat lost by the instrument.

e. The excess of the final temperature above the air.

I. The increment of temperature observed.

I^c. The increment corrected.

F. The weight of the fluid.

Vss. The value of the apparatus in terms of the fluid.

X. The value of the instrument in terms of fluid.

Distilled Water.

	I.	II.	III.	IV.	V.
D.	132°·0	131°·7	132°·8	132°·5	132°·8
e.	1·1	0·3	0·4	1·4	2·2
I.	6·38	6·45	6·46	6·40	6·40
I^c.	6·39	6·44	6·45	6·43	6·45
F.	1234·5	1234·5	1234·5	1234·5	1234·5
Vss.	55·5	55·5	55·5	55·5	55·5
X.	62·45	62·60	62·65	62·60	62·65

Mean value in terms of water 62·59.

Solution of Sulphate of Potash (100 parts contain 2·18 salt).

	I.	II.	III.
D.	131°·8	132°·2	132°·4
e.	1·3	1·1	1·0
I.	6·38	6·42	6·45
I^c.	6·41	6·43	6·46
F.	1264·5	1264·5	1264·5
Vss.	57·0	57·0	57·0
X.	64·27	64·28	64·48

Mean value in terms of solution 64·34.
Specific heat 0·973.

Solution of Nitrate of Potash (100 parts contain 2·53 salt).

	I.	II.	III.
D.	135°·8	135°·5	135°·7
e.	1·1	1·4	1·0
I.	6·59	6·56	6·57
I^c.	6·60	6·59	6·58
F.	1264·5	1264·5	1264·5
Vss.	57·0	57·0	57·0
X.	64·23	64·27	64·08

Mean value in terms of solution 64·19.
Specific heat 0·975.

Solution of Chloride of Potassium (100 parts contain 1·86 salt).

	I.	II.	III.	IV.
D.	132°·8	132°·4	132°·3	132°·4
e.	1·6	1·6	1·6	1·6
I.	6·45	6·43	6·42	6·43
I^c.	6·48	6·46	6·45	6·46
F.	1264·5	1264·5	1264·5	1264·5
Vss.	57·0	57·0	57·0	57·0
X.	64·48	64·48	64·43	64·48

Mean value in terms of solution 64·47.
Specific heat 0·971.

Solution of Acetate of Potash (100 parts contain 2·45 salt).

	I.	II.	III.
D.	133°·5	132°·9	133°·1
e.	1·8	2·1	1·8
I.	6·46	6·44	6·46
I^c.	6·50	6·49	6·50
F.	1264·5	1264·5	1264·5
Vss.	57·0	57·0	57·0
X.	64·34	64·53	64·54

Mean value in terms of solution 64·47.
Specific heat 0·971.

III. *A description of an extensive series of the Water Battery; with an Account of some Experiments made in order to test the relation of the Electrical and the Chemical Actions which take place before and after completion of the Voltaic Circuit.*

By JOHN P. GASSIOT, *Esq.*, *F.R.S.*

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1. IN a paper, which I communicated to the Royal Society in 1839, and which was honoured by insertion in the Transactions of the following year, I described a series of experiments made with some powerful voltaic batteries, for the purpose of determining the possibility of obtaining a spark *before* the completion of the voltaic circuit. I was therein enabled to establish a few facts respecting polar tension, or rather respecting the absence of any notable degree of it in the batteries I described*; for instance, I proved that, with 320 series of Professor DANIELL's constant battery, polar tension was not evinced adequate to the striking distance of $\frac{1}{1000}$th of an inch; nor was I more successful in obtaining it with a water battery of 1024 series†, constructed by the same gentleman. I also stated that, according to the present theoretical views of the action of the voltaic battery, with the apparatus I then used, it ought to have taken place; and that, if by a still more powerful apparatus it could not be obtained, the theory must, in some way or other, be incorrect.

2. The preceding negative facts are not without their value in a scientific point of view; they show us, at least, a certain limit within which the anticipated effects could not be obtained. At the same time I could not fail to admit that they were anything but conclusive, as to the actual question of the possibility of obtaining the spark before the circuit was completed. That I am justified in calling the spark, under such circumstances, an anticipated effect, may be fairly assumed, because every electrician is aware that the terminals of a voltaic series invariably evince a certain amount of tension‡; and as spark is but a consequence of tension exalted to a maximum, it is only fair to anticipate that, by increasing the tension, it would be obtained.

3. A short time after the publication of the paper to which I have alluded, a communication reached me from my friend Mr. CROSSE, of Broomfield, Somersetshire, wherein he stated that, with 1626 cells of copper and zinc, excited with river water, he had succeeded in obtaining a spark between slips of tinfoil pasted on sealing wax. This communication I immediately forwarded for publication in the Philosophical Magazine for September 1840.

* Philosophical Transactions, 1840, p. 184, § 10. † Ibid. § 15. ‡ Ibid. § 14.

4. I was at that time engaged in the construction of an extensive series of the water battery; but, from the difficulties of insulation, which continually presented themselves, considerable time elapsed before the battery was in a condition to afford results, on which any dependence could be placed. Having, at length, to a certain extent, surmounted these difficulties, I have been enabled especially to study the character and action of the water battery, and through it, I may hope, of the voltaic battery generally. The results of my experiments, with a description of the apparatus used, may, I think, not be uninteresting to the electrician, particularly as they establish the fact, beyond any doubt, of not only the passing of a distinct spark before the completion of the circuit, but the practicability of continuing this action for several weeks in constant succession, and enabling us to examine, with much accuracy, the rationale of the action of this extraordinary apparatus.

5. The water battery, which I have constructed, and which I am about to describe, consists of 3520 pairs, or series of copper and zinc cylinders, each pair being placed in a separate glass vessel, well covered with a coating of lac varnish. The glass cells are placed on slips of glass, covered on both sides with a thick coating of lac; this coating being fixed by heating the glass over a gas furnace, and then covering it with the varnish. The 3520 cells, thus insulated, are placed on forty-four separate oaken boards, also covered with lac varnish, each board carrying eighty cells. The boards, or trays, slide into a wooden frame, where they are further insulated by resting on pieces of thick plate glass, similarly varnished.

6. It may at first sight appear that many of these precautions are unnecessary; in truth, had I, at the outset, expected they would have been requisite, I might probably have been deterred from attempting so troublesome and lengthened an inquiry. At first I imitated the apparatus of Mr. Crosse, already referred to (3.), the copper cylinders being made water-tight that they might themselves constitute the cells; and considering such insulation would be sufficient, I attached the cells to the boards with sealing wax, poured into holes made in the boards for the insertion of each cell. I found this arrangement answer very well for a few hundred series, but when the number was augmented, and the battery completed, the insulation was sadly deficient. This induced me to take the battery asunder, and to have distinct or separate glass vessels made for each pair. After again completing the entire series, I found the insulation was even less efficient than before; for from the glass attracting moisture from the atmosphere, as well as from the evaporation of the battery, each cell became a conductor, and scarcely any effect could be produced on the *electroscope*; in fact, it was not until I had finally adopted the arrangements I have previously described, that any approximation to a tolerable insulation could be maintained.

7. The general appearance of the battery may be seen by referring to Plate I. fig. 1, where A, A′ represent the wooden frames, in which are placed the forty-four boards containing the entire battery; B a shelf on which a galvanometer can be placed, or any other apparatus for the detection of a current or chemical action.

N and P are the terminals or poles of the battery. Fig. 2 is a single cell; *g*, a glass vessel; *c*, copper; *z*, zinc. Fig. 3, one of the boards as it appears when removed from the entire series. Fig. 4, a double electroscope. Fig. 5, a HARRIS's single-leaf electroscope. Fig. 6, another electroscope, having two separately insulated gold leaves, *b b'*: in addition, I used a delicate galvanometer, and a solution of iodide of potassium for the detection of currents and of chemical action. The battery was charged, by carefully filling each cell with rain water.

8. With all the precautions I have described, the insulation of the battery was still imperfect; and, from the experience which I have gained during the construction of this apparatus, I have little hesitation in asserting, that the very nature of the water battery must prevent the experimentalist from obtaining insulation for any lengthened period, when such an extended series is employed.

9. In proceeding to describe the effects which this apparatus has presented, I must endeavour to draw a distinct line of demarcation between the *static* and the *dynamic* effects; for although these are, in a certain sense, both associated in some forms of electric development, yet as I have been enabled in a degree to isolate them here, it is my intention to regard them separately.

10. We know, from the very earliest experiments, that the extremities of a voltaic pile present opposite electrical states; it is therefore stating no new fact, to say that when one extremity of the series is connected with the ground, the other, on being connected with a gold-leaf electroscope, indicates a high degree of electric tension, and that the gold leaves diverge with considerable energy. Indeed, in the battery above described, there was little need of making connection with the ground; for, with all my precautions, I found the insulation was in a short time very imperfect, and that, by this communication with the earth, a complete circuit, to a certain extent, already existed.

11. As the *static* effects present themselves antecedently to the *dynamic*, they necessarily demand the first notice. The entire battery was connected in one series, and copper wires from the extreme cells were connected with the plates *a* and *b* of the double electroscope (fig. 4); this instantly produced a considerable and steady divergence of the gold leaves; and, on applying the usual tests, the plate *b*, connected with the copper extremity, gave signs of vitreous, and *a*, connected with the zinc, of resinous electricity. If *a* was connected with one extremity of the battery, and the other extremity was connected or not with the ground, the same general effects occurred; the divergence of the leaves corresponded with the connection, and the leaves of *b* diverged by induction; if, in this state, *b* was touched and then removed from the influence of *a*, it was found charged with the opposite electricity.

12. These inductive effects were obtained under other forms; for instance, the condensing plate (*p*), which had been removed during the preceding experiments, was opposed to the charged plate *a*. When *a* alone was connected with the battery, and *p* was touched, while under the influence of induction, and then removed,

p was found oppositely charged; as was also an insulated carrier ball, when similarly treated.

13. The plate *a* of the electroscope (fig. 4) being retained in connection with one end of the battery, a piece of very thin mica was laid on it; on this mica rested a wire W proceeding from a single-leaf electroscope (fig. 5), the disc (*d*) of which was in connection with the earth by means of a wire; with this arrangement the gold leaf was electrified by induction, and struck against the disc (*d*); glass, lac and sulphur were in turn substituted for the mica, and the same general effects resulted. The same battery connection was maintained, the electroscope (fig. 5) being disconnected. An insulated carrier ball was successively applied to the plate *a*, and an unlimited succession of charges could be carried and accumulated to another electroscope: these charges were with equal facility obtained when the *direct* connection between the battery and the earth was broken; the insulation of the battery was, however, comparatively imperfect; and I shall therefore have occasion to revert to some of these results which I afterwards obtained less in degree, but equally definite in character, from a portion of the battery detached for the purpose of more efficient insulation; for the present we need only allude to those effects, which do not absolutely involve the perfect insulations of the battery itself. When a Leyden jar, held in the hand, was subjected to the action of one end of the battery, a charge was readily accumulated, and, of course, still more favourably by means of a mica battery. When the coatings of a Leyden battery, consisting of twelve jars, with a surface of sixteen feet, were connected with the respective ends of the series, the accumulation of tension was considerable.

14. With the entire battery, the tension was so great, that the leaves of a gold-leaf electroscope diverged when that instrument was placed within two or three inches of either end of the battery, or over any of the terminal cells. Advantage was taken of this to test, whether any effect of tension could be observed when the circuit was completed; but the instant this was effected, the leaves of the electroscope as instantly collapsed, nor could I detect, either by the aid of the condenser, or otherwise, the slightest trace of tension; it, however, immediately reappeared when the circuit was again broken.

15. Thus far I have been examining the *static* effects of a moderate amount of tension, similar in kind to those which have been long familiar to the electrician, but modified so as to produce inductive effects, differing in some degree from any elsewhere recorded. My first experiment, after making every allowance for loss of electricity, or, as it would be better to express it, loss of tension through insufficient insulation, admits but of one interpretation: the interpretation itself is generally allowed, but the force of it is not, I believe, generally admitted; it is, *that the elements constituting the voltaic battery, when arranged in series, assume polar tension before the circuit is completed*; and that in the apparatus above mentioned, this tension is such *that a spark will pass before the circuit is completed.*

16. When the micrometer electrometer, described in my former paper*, was introduced between the terminal wires, sparks, through the space of $\frac{1}{80}$th of an inch, were obtained; and when the double electroscope (fig. 4) was included in the circuit, and the discs *a* and *b* were approximated, an uninterrupted succession of sparks would pass between the discs. These effects, which I have repeatedly shown to many friends, are most brilliant. On one occasion they were continued uninterruptedly day and night for upwards of five weeks; and although some months have now elapsed since this battery was completed, it still exhibits the same effects.

17. When the experimenter was standing on the ground, and consequently, as has been already explained, in actual, although imperfect connection, with the battery, he could draw sparks from either terminal. We shall, in the sequel, be enabled to trace, with more precision, the rise of this tension; for the present, we are only concerned in establishing its existence, and thereby proving the first fact, that *tension* or *electrostatic effects precede, and are independent of, the completion of the voltaic circuit.*

18. Hitherto we have not obtained any insight into the condition of the *dynamic* effects under such circumstances of antecedent tension. For testing the presence of what is usually termed the current, or in other words, obtaining the means of observing the electro-dynamic effects, I used the instrument which is best suited for examining such phenomena, and which invariably attests the instant completion of a voltaic circuit. An exceedingly delicate galvanometer was introduced at B (see fig. 1), and the two condensing plates *a* and *b* of the double electroscope (fig. 4) were respectively attached by wires to the terminals N and P of the battery, fig. 1. If great care was taken not to make any connection with the ground, the party manipulating being himself well insulated on shell-lac, no action could be perceived on the needle in the galvanometer, although the gold leaves of the electroscope immediately diverged to a very considerable extent.

19. This experiment was, however, of too much importance to be passed over without adopting every means of making it unexceptionable. Two trays from the battery, being a series of 160 cells, were removed and insulated, by being supported on stout varnished glass pillars twelve inches high; the whole being placed upon an Arnott's stove in which a fire had been kept burning for several hours. The galvanometer was interposed between the zinc terminal of one tray and the copper terminal of the other; and the extremities of this reduced series were arranged so as to exhibit the same effects of electric tension which we have seen in the entire series; but not the slightest indication of dynamic action could be detected by the galvanometer. The action of the instrument I used could not be in fault; and some idea may be conceived of its extreme delicacy, when I state that, with one cell of the gas battery† I have obtained a steady deflection, whilst a resistance of twelve miles of thin copper wire was interposed in the circuit; when the electroscope (fig. 6) was used, *c c'* being respectively connected with N and P of battery, the gold leaves *b b'*, were attracted;

* Philosophical Transactions, 1840, p. 184, § 12. † Ibid. 1843.

and the moment they touched each other, the needle of the galvanometer was deflected.

20. The best definition that occurs to me of a current is that given by FARADAY in his Third Series of Experimental Researches*. "By current I mean anything progressive, whether it be a fluid of electricity, or two fluids moving in opposite directions, or merely vibrations; or, speaking still more generally, progressive forces;" and in juxtaposition to this, he says†, "If the magnetic effects depend upon a current, then it is evident they could not be produced in any degree before the circuit was complete, because prior to that no current could exist." Now it is manifest that, in the experiments already mentioned, the voltaic elements have the power of exhibiting electric effects at either, and both ends or terminals, before any progression or actual perceptible force takes place in the course of the series; in other words, that *static* effects exist before or independently of currents, but that these effects cease immediately on currents being developed.

21. But, in an inquiry like this, we must examine more closely the actual chemical action; for it involves much of the source of controversy between the contact and chemical theories; and I was naturally anxious to discover whether simultaneously with these *static* effects, or perhaps antecedently to them, *any chemical action took place in the cells of the battery*; and if so, to what amount.

22. FARADAY‡, in the course of that branch of his experimental researches which introduced into notice the voltameter, established the most accurate means of measuring the amount of chemical action in the battery cells, by the equivalent amount of chemical decomposition exhibited in that instrument; he has also directed our attention to the fact, that this amount of electro-chemical decomposition depends essentially on the current as denoted by the galvanometer. There was every reason, with these facts before us, to expect that the battery, which did not produce a current, would not evince any degree of chemical decomposition. Recourse was, however, had to the test of experiment; and, instead of introducing the galvanometer, I substituted for it a small piece of bibulous paper, saturated with a solution of iodide of potassium; the gold leaves of the electroscope diverged as before, but, however long the duration of action, not the least indication of the liberation of iodine was perceptible. The inference I make from this is, that no definite chemical action took place in any cell of the battery, and consequently that the *electric effects* above shown, and which are termed *static* effects, take place *before* or *independently of the actual development of the chemical effects.*

23. I am aware that, in some form or other, this fact has been acknowledged by the most strenuous advocates of the chemical theory. BECQUEREL§ thus adverts to it:—"We must conclude, from all the electrical phenomena, that, in almost all cases, a chemical action has taken place; and hence we are led to believe that the latter is the cause which exercises the greatest degree of influence over their production; nevertheless,

* Experimental Researches, § 283. † § 282. ‡ § 510. § Traité de l'Elect., vol. ii. p. 145; vol. v. p. 3.

in the present condition of science, we must not yet abandon VOLTA's theory, since it may very readily happen, that, at the contact of two bodies, a disengagement of electricity may take place, resulting from a commencement of chemical action between these bodies."

DE LA RIVE*, who has laboured perhaps more than any of the continental philosophers in advocating the chemical origin of voltaic electricity, cannot but admit some such similar qualification, as may be seen from the following extract from one of his papers:—"The two theories between which philosophers are divided with respect to the origin of voltaic electricity, are still the subject of lively controversy; when we are adverting to the pile itself and to hydro-electric currents, we cannot deny the superiority of the chemical theory; the recent labours of FARADAY have, moreover, added powerful arguments in favour of this theory; but it must be acknowledged that it is not easy to defend it when we advert to electricity of tension developed in the contact of two heterogeneous bodies, especially if the two bodies are solid."

FARADAY†, who has recently instituted a series of elaborate researches in support of the chemical theory, writes thus of it:—"The theory assumes that the particles of the di-electric (now an electrolyte) are, in the first instance, brought by ordinary induction into a polarized state, and raised to a certain degree of tension or intensity before discharge commences, the inductive state being in fact a *necessary preliminary* to discharge." Again, "One point is, that different electrolytes or di-electrics require different initial intensities for their decomposition. This may depend upon the degree of polarization which the particles require before electrolytic discharge commences‡."

GROVE§, in a recent communication to the Royal Society, in allusion to the action of the gas battery, says, "If, indeed, the contact theory assume contact as the efficient cause of voltaic action, but admit that this can only be circulated by chemical action, I see little difference, save in the mere hypothetical expression, between the contact and chemical theories; any conclusion which would flow from the one would likewise be deducible from the other; there is no observed sequence of time in the phenomena, the contact or completion of the circuit and the electrolytical action are synchronous. If this be the view of contact theorists, the rival theories are mere disputes about terms. If, however, the contact theory connects with the term *contact* an idea of force which does or may produce a voltaic current independently of chemical action, a force without consumption, I cannot but regard it as inconsistent with the whole tenor of voltaic facts and general experience."

24. I shall have occasion to revert to the gas battery, the action of which is fully described in the paper from which I have taken the preceding quotation; but the action we are now examining is not that arising from *contact or completion of the circuit*, but that which is caused by contact in the arrangement of a progressive

* Archives de l'Electricité, vol. i. p. 619.

† Experimental Researches, § 1345.

‡ Ibid. § 1354.

§ Philosophical Transactions, 1843.

series of the elements of a voltaic battery *previous* to the circuit being completed; such progressive arrangement being indispensable for the production of the effects we are now examining, or the production of certain forces in a given direction. A mere heterogeneous assemblage of the elements will not produce the effects; on the contrary, any alteration in the regular series produces a corresponding reduction of force, and any number of batteries arranged—copper, liquid, zinc,—will exactly neutralize the action of a similar number arranged,—zinc, liquid, copper.

25. The question I am now examining is, however, not whether contact produces current, but whether it produces electric development, and whether that development is accompanied by any chemical action; and this necessarily involves the question, whether the effects of current, or those usually called voltaic, have the same efficient cause as the electro-static. That certain effects can be produced independently of any *apparent* chemical action, is not merely proved by experiment with the water battery, but it is further confirmed by many unexceptionable experiments; among those for which I may particularly claim attention, are those of M. Peclet, who in describing them says, "I have only had in view static electricity developed by contact, I have not troubled myself about currents when the circuit is closed*."

26. The examination of M. Peclet's experiments, the investigation of the action of the voltaic series generally, and more particularly of the water battery, seem to lead to the inference that elective affinity is greatly concerned in the *antecedent* action, of which chemical combinations, when the circuit is closed, are the *consequence*. I might quote the particular experiments of M. Peclet as an evidence of static effects having been obtained without any apparent chemical combination; but, without attempting to follow out what may, perhaps, somewhat fairly, be assumed as hypothetical cases, viz. those in which tension does not appear to terminate in chemical action, *let us trace the process by which tension rises in an insulated pile, and the still further process necessary to establish a current.*

27. Two trays of the battery were carefully insulated as before (19.): if in this state one of the piles is touched by the hand, its electric tension is apparently destroyed, the leaves of the electroscope in connection collapsing; whilst those of an electroscope attached to the other terminal obtain their extreme divergence. If this battery be now left to itself, the end which has been touched regains a certain amount of tension, and the leaves of the other electroscope collapse in proportion: generally, the means of raising the tension of one extremity of the battery is to touch the other. I do not mean to assert that the tension of the end which was touched is entirely destroyed, but certainly with 160 series, for the space of several seconds, I could not with the most delicate gold-leaf electroscope obtain the slightest indication of it.

28. Marianini went through a series of experiments, in which he found that in no case was tension actually destroyed; but that it fell in proportion to the duration of the time during which the circuit had been completed. My object now was not, however,

* Archives de l'Electricité, vol. i. p. 622.

to complete the circuit; for I wished to test an intermediate stage between actual insulation and actual completion of circuit, in order to discover the character of the discharges effected by touching the respective terminals, or rather their influence over the state of tension, into which the whole series was thrown. I wished, for instance, to discover whether the discharge I effected, threw the elements of the battery *back*, into the normal condition which prevailed antecedent to the discharge; or whether it threw them *forward* by completing the act of chemical combination, the preparatory state of which already existed; whether, for instance, mere discharge, either by the earth or by completion of the circuit, for an instant, is one small fraction of a current; and, if so, whether a current is not really a collection of discharges of electricity of tension.

29. For this purpose the following experiments were made: a copper wire attached to N of the battery was connected with the galvanometer, and this with the plate *a* of the double electroscope, fig. 4. A platinum wire was attached to P of the battery, the end of which rested on a piece of bibulous paper saturated with a solution of iodide of potassium: another platinum wire, also resting on the paper, was connected with the other plate *b* of the electroscope; by the mechanical arrangement of this instrument, the plates could be approximated or separated as required. Fig. 7 shows the arrangement; N and P, the terminals of the battery; G, the galvanometer; *a* and *b*, the plates of the electroscope; S, solution of iodide of potassium.

30. When the plates *a* and *b* were approximated so as to permit sparks to pass at intervals of about a second, a *tremulous* motion was imparted to the needle; but when they were brought so nearly in contact as to permit the discharges to take place in quick succession, the needle was *steadily* deflected, and iodine freely evolved; proving that chemical action was occurring in each cell, and that the current is a collection or an accumulation of discharges of electricity of tension; for although the circuit was completed by distinct and separate discharges, still the deflection of the needle was as steady as if the discs had been in actual metallic contact.

31. The discs *a* and *b* were then separated to the distance of about an inch; a piece of tinfoil was suspended by means of a thread of white silk; the tinfoil vibrated between the plates, but no effect could be produced on iodide of potassium or on the galvanometer.

32. I have already alluded to the extreme difficulty I experienced in effecting perfect insulation. I was anxious to ascertain whether this insulation, and at the same time a high state of intensity, could be obtained, and whether, in such a state, any evidence of chemical action could be detected when one end of the battery was in connection with the ground. After many trials, I succeeded in insulating 320 cells; and so efficient was even this reduced number in point of intensity, that sparks could be obtained by means of the micrometer electrometer through a space of $\frac{1}{1000}$th of an inch. The ends of two platinum wires were then fixed so as to rest on a piece of bibulous paper saturated with a solution of iodide of potassium. One of the

wires was connected at one time with the copper, and at another time with the zinc terminal of the battery; while the wire attached to the other extremity was connected with the earth. This arrangement being continued for several hours, and the paper kept constantly moist, not the slightest evidence of any evolution of iodine could be detected, until by a momentary contact made with the further extremity of the battery and the ground, either by a wire, or by touching it with the hand, the circuit was completed. Here we have a voltaic battery the intensity of which is sufficient to elicit a *spark* between its terminals before the circuit is completed, but in which antecedent thereto, the slightest chemical action is not appreciable; and this when one end is in connection with the earth, and consequently having the intensity exalted to a maximum short of actual discharge.

33. I am aware of the many forms the contact theory has assumed since Volta first propounded it; nor can we lose sight of the many errors which his successors have committed in attempting to follow out their favourite views of metallic contact and electro-motive forces. I am indebted for much information on this point to the kindness and industry of Mr. C. V. Walker, who has occupied much time in procuring me references to the researches of those electricians already alluded to, as also to a long list of others whose names adorn the pages of science. I could easily have added to those I have named, by referring to the experiments of many other authors who consider that their favourite theory of contact has been fully established. It is not, however, my object to advert to these speculations: we have before us certain facts connected with the action of the voltaic battery; first *contact*, or successive juxtaposition, and simultaneously with it, effects of *tension*; then the completion of the circuit, and simultaneously with it, *development of chemical action* and *current*; but in all these cases contact is first in order, developing tension. Becquerel describes it by stating, "When two bodies are in contact the affinities commence exercising their action before combination takes place." M. De la Rive, "The electricity of tension developed by contact of heterogeneous bodies." Faraday, "That the particles of the electrolyte are brought into a polarized state, and raised to a certain degree of tension, before discharge takes place:" but I am not aware that there are any *experimental* facts to prove whether this tension in the voltaic battery, which itself is of an opposite character at each terminal, and, as we have seen, can be exalted so as to produce discharges in the form of sparks for many weeks' constant duration (16.), is due to the chemical constituents of the battery, or to mere contact of dissimilar bodies, without reference to their chemical affinities. I was therefore most anxious to see whether some experiment could not be devised, which would test the action in a satisfactory manner, and for this purpose I availed myself of an extended series of Grove's gas battery, described by him in a paper already alluded to (23.)*.

34. The elements used in this form of the voltaic battery consist of two gases and one metal; with fifty series charged with oxygen and hydrogen, it is stated that the

* Philosophical Transactions, 1843.

gold-leaf electroscope was notably affected. The instrument used by Mr. Grove, whose original experiments I had the pleasure of witnessing in the laboratory of the London Institution, was the same as is represented in fig. 6. Nothing can be more decisive than that the *static* effects of the voltaic battery are not due to the contact of dissimilar *metals*; as in this arrangement, only one metal, platinum, is used; but this battery, whose action is, in itself, so purely chemical, presents to us a full corroboration of the *static effects preceding the development of chemical action.*

35. A series of forty cells, the same as are described in Mr. Grove's paper*, were charged with oxygen and hydrogen; these sensibly affected the gold-leaf electroscope, fig. 3. This arrangement was kept charged for upwards of three months. No decrease in the gas of the oxygen tubes could be detected. Whenever the terminals were tested by the electroscope, they invariably exhibited the usual signs of tension; but not the slightest chemical or dynamic effect could be obtained until the entire circuit was completed.

36. Here we have a battery, the active elements of which are two gases, which, with a closed circuit, immediately enter into active chemical combination; remaining for upwards of three months in such a state of tension as at all times to affect the leaves of an electroscope; but in which no amount of chemical action could be detected whilst the circuit remained open.

37. It now became a matter of some interest to ascertain, *first*, the minimum amount of series with which the gas battery charged with oxygen and hydrogen would exhibit static effects; and, *secondly*, whether, when it was charged with gases which do not enter into chemical combination, *any* signs of tension could be elicited.

38. By careful arrangement I obtained an attraction in the gold leaves of the electroscope (fig. 6) with a series of nine pairs; with twelve or fourteen, the effects are very distinct, and required no very delicate manipulation. The series of forty pairs was then charged with oxygen and nitrogen; at first the electroscope was affected, and chemical action as well as dynamic effects were obtained with the closed circuit; these, however, were evidently due to impurities in the nitrogen (this gas was obtained by burning phosphorus in common air; the oxygen by electrolysis): after keeping the circuit closed for two days, these effects ceased, when not the slightest static, chemical or dynamic actions could be detected; the volumes of the gases remaining perfectly stationary, whether the circuit was closed or open.

39. From the preceding experiments we learn that, when the gases used in this battery are oxygen and hydrogen (which will from their affinity for each other enter into chemical combination), a series of ten or twelve is sufficient to develope static effects; but that, when charged with gases which have not this power, viz. oxygen and nitrogen, even a series of forty does not affect the electroscope.

40. The advantage of using oxygen and hydrogen is, that although the hydrogen is slightly absorbed by local action with the atmospheric air in the solution, action

* Philosophical Transactions, 1843, plate 5. fig. 1.

does not take place in the oxygen tubes until electrolysis commences; and we have thus the most correct means of defining our results.

41. With hydrogen and chlorine, signs of tension were obtained with a series of six pairs of cells.

42. With chlorine in a single tube, and amalgamated zinc as the positive element, a combination by which, as Grove has shown*, one pair will decompose water, a series of two pairs affected the electroscope.

43. Having thus elicited that for the purpose of obtaining static effects with a gas battery, it is indispensable that the two gases employed be capable of entering into chemical combination with each other, and having found that the higher the state of their mutual chemical affinities, the less was the number of series required to produce static effects, my attention naturally reverted to the older forms of the voltaic battery. I allude to those having two metallic elements excited by acid solutions.

44. Ten of the glass cells of the water battery (5.) were filled with dilute sulphuric acid. In each cell I placed a small porous earthenware vessel, also filled with the same solution. The metallic elements in this arrangement were amalgamated zinc and platinum; the latter being placed in the porous vessels, each cell was carefully insulated. This arrangement affected the leaves of the electroscope (fig. 6), while it required sixteen series of the water battery (5.) to produce the same effect.

45. The dilute acid was then removed from the porous vessels, and these were refilled with strong nitric acid, forming the well-known nitric acid battery of Grove. Three series of this arrangement affected the electroscope, and with the assistance of a Zamboni's pile, *distinct signs of tension could be elicited from a single pair*; the platinum showing vitreous and the zinc resinous electricity.

From the preceding experiments it appears, that to obtain evidence of tension, the principal requisite is good insulation, and that this condition being fulfilled, the most energetic chemical battery will exhibit signs of tension before the completion of the circuit with a smaller series than that which is merely excited with rain water (44. 45.).

Conclusion.

The deductions which I make from the experiments described in this paper are as follows:—

1st. That the elements constituting the voltaic battery assume polar tension before the circuit is complete (10. 11. 15.) even in a single cell (45.); and that the existence of this polar state is demonstrated by the action on the electroscope being different at each terminal of the battery.

2nd. That this tension, when exalted by a series of pairs, is such, that a succession of sparks will pass between the terminals of the battery before their actual contact (16. 32.).

3rd. That these static effects precede, and are independent of, the completion of

* Philosophical Transactions, 1843, p. 103, Note.

the voltaic circuit (10. 11. 17.), as well as of any *perceptible* development of chemical or dynamic action (18. 19.).

4th. That when the circuit is completed, whether by actual contact of the terminals, or merely by approximating them, so as to allow a succession of sparks, the dynamic effects on the galvanometer are the same (30.); each producing a steady deflection of the needle; consequently that the current, even when the circuit is closed, may be regarded as a series of discharges of electricity of tension, succeeding each other with infinite rapidity.

5th. That the rise of tension in a battery (the chemical affinities of its elements being feeble, as in the water battery) occupies a measurable portion of time (27.).

6th. That to produce *static* effects in the voltaic battery, it is indispensable that the elements should be such as can combine by their chemical affinities (34. 35.), that the higher those chemical affinities are exalted, the less is the number of elements required to exhibit the effects of tension (38. 39. 41. 42. 44 and 45.), and consequently, that the *static* effects elicited from a voltaic series are direct evidence of the first step towards chemical combination or dynamic action.

The chemical effects, when obtained in the generality of the experiments described in this communication, are of course feeble; but they are precisely the same in character as those exhibited by the more powerful voltaic combinations; and it may fairly be concluded that the rationale of each is the same, and that they only differ in the degree of action.

Received April 12, 1844.

Note.—I have recently constructed an instrument, by means of which the tension in a single series of the voltaic battery can with facility be tested without the aid of Zamboni's pile. Fig. 8 represents the electroscope, in the construction of which I was in a great measure indebted to an apparatus described by Dr. Hare*. A is a glass vessel, the stem of which is well-coated with lac; B, B′, two copper wires passing through glass tubes and corks; D, D′, gilt discs, each about two inches diameter, attached to the wires; P, a copper plate with a wire passing through a glass tube; to the end of the wire is attached a *narrow* strip of gold leaf, L. The discs must be adjusted with care, so as to allow the leaf to be equidistant from each. If B is connected by a wire attached to the platinum, and B′ by another wire attached to the zinc of a single cell of the nitric acid battery, insulated on a plate of lac, and an ex-

* Silliman's Journal, vol. xxv.

cited glass rod is approximated very gradually towards the plate P, the gold leaf will be attracted to B′, or the disc attached to the zinc; and if excited resin is approximated in a similar manner, the leaf is then attracted to B, or the disc attached to the platinum. By means of this instrument, my friend, the Rev. CHARLES PRITCHARD, obtained signs of tension in a single cell excited by dilute sulphuric acid with platinum and zinc. This experiment I subsequently verified, and obtained similar results with single cells of other usual arrangements of the voltaic battery; but in all the experiments I made, the higher the chemical affinities of the elements used, the greater was the development of the evidence of tension.

March 1844.

IV. *On the Existence of Phosphoric Acid in Rocks of Igneous Origin.* By GEORGE FOWNES, *Ph. D., Chemical Lecturer in the Middlesex Hospital Medical School. Communicated by* THOMAS GRAHAM, *Esq., F.R.S., &c. &c.*

Received April 17,—Read April 25, 1844.

THE important although obscure functions attributed to the elementary body phosphorus, both in the vegetable and in the animal kingdoms, and the well-known fact that rocks of nearly every description afford on disintegration soils more or less capable of supporting the life of plants, and from which consequently phosphoric acid cannot possibly be absent, seemed to render a search for that substance in rocks of igneous origin generally very desirable, because if there found, an easy and satisfactory explanation of the origin and first source of the element in question would be given. As I am not aware that any direct researches on this subject have yet been made, or at least placed on record, I venture to submit to the notice of the Royal Society the results of a few experiments made by myself, which, so far as they go, resolve the question in the affirmative.

The first substance tried was the fine white porcelain-clay of Dartmoor, Devon, the result of the disintegration of the felspar of the granite of that district. This is one of the chief components of porcelain and of the finer kinds of English earthenware, and was found on analysis to correspond very closely in composition with that of the material employed in the manufacture of the Sèvres porcelain. It was thought that phosphoric acid, if present, would be in combination with a portion of the alumina; and as the phosphate of that earth is readily soluble in dilute mineral acids, while the silicate offers great resistance to these agents, mere digestion with acid would suffice to extract the whole, or the greater part of the phosphate, which could be afterwards precipitated by an alkali, and examined.

With this view, 1000 grains of the clay were boiled during several hours in a flask with a quantity of pure dilute hydrochloric acid; a large bulk of distilled water was then added, and the whole allowed to rest until perfectly clear. The acid liquid was then carefully decanted from the undissolved clay, evaporated in a porcelain basin to a small bulk, and precipitated by a slight excess of pure ammonia. The scanty, reddish precipitate obtained, which consisted chiefly of alumina and oxide of iron, was collected upon a little filter, thoroughly washed with distilled water, dried, and ignited. It was next reduced to fine powder, and mixed with an equal weight of pure silica in a finely-divided state, and six times as much anhydrous carbonate of soda. This mixture was heated to fusion in a platinum crucible. When cold, the melted

mass was acted upon by boiling water, and the soluble and highly alkaline portion separated by a filter from the insoluble silicate of alumina. The solution was mixed with excess of nitric acid, evaporated to dryness, water added, and the product filtered. The liquid thus obtained was divided into two portions; one of these was carefully neutralized by a little ammonia, and mixed with a few drops of solution of nitrate of silver; a distinct yellow precipitate appeared, which was freely soluble in dilute nitric and in acetic acids. The second portion was mixed with excess of ammonia and some hydrochlorate of ammonia, and a few drops of solution of sulphate of magnesia added. After a short interval, a crystalline, granular, white precipitate, the ammonio-magnesian phosphate, made its appearance, which increased in quantity by agitation.

This experiment, which demonstrates the presence of a small quantity of phosphoric acid in the clay, in a most unequivocal manner, was several times repeated with a like result. The purity of the acids, carbonate of soda, and other materials employed, were rigorously tested, and filtration through paper of the original acid liquid purposely avoided, lest a trace of earthy phosphate should have been dissolved from the paper.

The porcelain-clay is extracted from the disintegrated granite by mere washing with water, and subsidence, and the water of the district in which it is found is, in all probability, exceedingly pure. It was thought worth while, however, to examine in the same manner the decomposed rock which had not been subjected to any artificial treatment, and a specimen taken by myself from the quarry was chosen for the purpose. The result showed the presence of phosphoric acid as in the clay, and apparently to about the same extent, allowance being made for the quartz-grains, mica, &c.

In the examination of unaltered felspar, I failed, unfortunately, in getting a conclusive result. The mineral, although reduced to very fine powder by trituration in a mortar of Swedish porphyry, was found to be so hard and dense as to resist completely the action of the acid at a boiling temperature. An insignificant quantity of oxide of iron was dissolved out, in which no phosphoric acid could be detected. 200 grains of the powdered felspar were then fused with a large excess of carbonate of soda; the mass was treated with water, filtered, the solution supersaturated with nitric acid, and evaporated to dryness; water was poured upon the residue, and the whole placed upon a filter. The solution was then examined, as before, for phosphoric acid, but with an indistinct and doubtful result. Too small a quantity of the felspar had been used, and the mass of nitrate of soda present interfered too seriously with the action of the tests to render their evidence of any value. A far better mode of investigation would be, to act upon the powdered mineral with hydrofluoric acid, in the manner recommended by some analysts in the examination of natural silicates containing an alkali; not being, however, in possession of the necessary platinum vessels, I was obliged to abandon the attempt.

Other substances were then tried with very decisive results. The method of proceeding adopted was very much the same as that already described. The minerals were very finely powdered in the porphyry mortar and boiled, as before, with dilute hydrochloric acid. All were much more readily attacked than the porcelain-clay, and yielded solutions containing a large quantity of alumina and oxide of iron. The liquid was separated from the insoluble part by decantation, evaporated nearly to dryness, water added, and then an excess of ammonia. The copious, bulky precipitates obtained were washed and digested in dilute acetic acid, which has the property of dissolving with great facility both oxide of iron and alumina, while it leaves untouched the phosphates of those bases. The undissolved residue was dried, ignited, fused with silica and carbonate of soda, and the product examined in the manner already described. The addition of silica is indispensable to the retention of the whole of the alumina in an insoluble condition. Phosphate of alumina is not decomposed by carbonate of soda by fusion, or only partially, and is besides soluble in an aqueous solution of that salt.

The results of the examination may be thus briefly stated:—

Dark grey vesicular lava from the Rhine, used at Cologne as a building-stone, being exceedingly strong and durable.—Enough phosphate of soda was extracted from 1000 grains of this substance to exhibit the yellow phosphate of silver, and the phosphate of magnesia and ammonia upon a large scale. The phosphoric acid might be said to be here *very abundant*, that is, comparatively speaking. No attempt was, however, made to estimate it quantitatively, as the operation is attended with great difficulty, and the result of doubtful value from the unavoidable errors of experiment bearing too large a proportion to the quantity of the substance.

White trachyte of the Drachenfels, near Bonn, on the Rhine.—This rock is apparently as rich in phosphoric acid as the preceding; nothing could be more distinct and satisfactory than the indications of the reagents.

Dark red, spongy, scoriaceous lava from Vesuvius.—This was tried in the same manner, and yielded *abundance* of phosphoric acid.

Compact, dark green basalt, or toadstone, *from Cavedale, Derbyshire.*—This substance was very tough, and difficult to powder. Enough phosphate of soda was, however, extracted from 750 grains of the rock to exhibit very unequivocally the characteristic tests described.

Dark blackish-green, extremely strong basalt from the neighbourhood of Dudley, termed *Rowley-ragg*, gave a very similar result. Phosphoric acid is not so plentiful in these substances as in the lava, although its presence is easily rendered evident.

An ancient porphyritic lava containing numerous crystals of hornblende, from Vesuvius.—The phosphoric acid was here very distinct, but not so abundant as in the more recent lava.

A specimen of tufa, or *volcanic mud*, also from Vesuvius, was found to contain phosphoric acid in notable quantity.

These were all the substances tried; they were taken, as is at once seen, indiscriminately from igneous formations of many localities and many ages, and they all, with one doubtful exception, in which practical difficulties interfered with the inquiry, yielded phosphoric acid. It is highly probable, therefore, that this substance is a very usual, although small, component of volcanic rocks.

It is not unlikely that the remarkable fertility possessed by soils derived from the decomposition of some varieties of lava may be, *in part at least*, due to the presence of this phosphate in the original rock, although much must of course be ascribed to the alkali, especially potash, which these substances contain, and which is gradually brought by the continued process of disintegration into a soluble state. There can be little doubt that the matter erupted from time to time from the interior of the earth, in a state of fusion, is thus destined to renew the surface from which the more valuable and more soluble components have gradually been removed by the action of water and other causes constantly in operation. If it should hereafter be found on a more extended investigation that phosphoric acid, although present in all igneous rocks, is most abundant in those of modern date, the fact will thus receive an explanation, the more ancient lavas having been most changed by the slowly-acting and almost imperceptible causes in question. One might be tempted to consider lava as a kind of fundamental material, from the subsequent alteration of which all others are derived, and expect it to contain, here and there at least, traces of all the elementary bodies known, even those most rare. In the present case, it cannot be altogether devoid of interest to trace to its first source the enormous quantities of phosphoric acid, for the most part locked up in a temporarily insoluble condition in the vegetable and animal kingdoms, and in the various strata of calcareous and sedimentary deposits, in the formation of which organized beings have played so prominent and so important a part.

6 *Coventry Street*,
April 17, 1844.

V. *Miscellaneous Observations on Animal Heat.*

By JOHN DAVY, *M.D., F.R.S., L. and E.*

Received November 2,—Read December 14, 1843.

1. *On the Temperature of the Pelamides* (*Pelamys Sarda*, CUV. and VAL.).

FISHES generally are commonly considered as cold-blooded. In a work published in 1839, I have stated particulars tending to show, that this commonly received opinion is not universally correct, and that fishes of the genus Thynnus, with some others of the Scomber family, may be inferred to be an exception*.

As this inference was founded chiefly on the reports of fishermen, it appeared very desirable to determine by actual thermometrical measurement what is the exact temperature of fishes of this family.

Hitherto, although watching for opportunities, and promised the aid of friends favourably situated, I have not been able to make any observations of the kind required, excepting on one species of these fishes, the Pelamides, the *Pelamys Sarda* of CUVIER and VALENCIENNES. The Pelamides, like most of its congeners, is migratory in its habits. In the early part of summer it appears in the sea of Marmora and the Bosphorus, and in August in the Black Sea, from whence, after spawning, it returns in September and October, on its passage to the Mediterranean. It is caught in the same manner as the Tunny.

In June 1841, whilst at Constantinople, I visited a fishing station for this fish, in an inlet of the sea of Marmora, and was present when a small capture was made, enabling me to ascertain the temperature of four specimens. This was done the instant they were taken out of the water, being in a boat alongside the net, by introducing a thermometer with a projecting bulb, through a small incision, into the muscle of the back, about an inch and a half, and immediately after into the cavity of the abdomen. In three instances, the thermometer in the back rose to 75° FAHR.; in one to 74°; in all, in the abdomen it rose to 73°. The Pelamides were of moderate size, between two and three feet long. The air at the time was 71°; the sea at the surface 68°; but probably at the depth from which the fishes were taken, it was a few degrees lower, the descending current of the Bosphorus then being, where coldest, at 62°.

Supposing that the water from which they were taken was 62°,—and it might have been lower, as the Pelamides swim in deep water,—the temperature of this fish would appear to be about 12° above the medium in which it swims, and at least 7° above that of the surface.

* Researches, Physiological and Anatomical, vol. i. p. 218.

This result seems in accordance with the inference, that all fishes are not cold-blooded. In the work already referred to, reasoning from the smaller size of the respiratory nerves of the *Pelamys Sarda*, compared with those of the Tunny, I offered the conjecture that its temperature would be found less than that of the Tunny, and somewhat higher than that of fishes of other orders with still smaller respiratory nerves, a conjecture which the observations described may be adduced as confirming.

In connexion with their temperature, my attention was directed to the blood of these fishes. I have been able to examine it only in three instances, and that partially, viz. the Sword-fish, the *Pelamys Sarda*, and the common Tunny. Considering the great difficulty there is in obtaining the subjects for experiment under favourable circumstances for examination, imperfect as were my results, I am induced to offer them now.

The Sword-fish appears to abound less in blood than the Pelamides, and the Pelamides less than the common Tunny; and accordingly the muscles of the former two are of a much lighter colour than those of the latter.

The blood of the Tunny is very rich in red particles: this is indicated not only by its appearance, but also by its specific gravity, which I have found as high as 1·070. The blood tried was taken from a fish, caught in the sea of Marmora, that weighed between two and three hundred pounds.

The blood of the Pelamides appears to be less rich in red particles than that of the Tunny, but more than that of the Sword-fish: I have not ascertained its specific gravity. The specific gravity of the blood of the Sword-fish I have found to be 1·051; the fish from which the blood was taken was caught in the Bosphorus, in the month of December, and was of large size.

Under the microscope the appearance of the red particles of the blood of these three fishes is very similar. They are commonly thin oval discs (very soft), containing oval nuclei: a few circular discs are intermixed with them. The medium dimensions of those of the Pelamides were about $\frac{1}{3000}$th of an inch by $\frac{1}{6000}$th; of the Sword-fish, about $\frac{1}{3000}$th by $\frac{1}{4000}$th; and of the Tunny, about $\frac{1}{5000}$th by $\frac{1}{8000}$.

That the red particles constitute that portion of the blood which is chiefly concerned in the production of animal heat, is now generally admitted. What a contrast appears, in comparing the blood of the fishes under consideration, with that of some of the colder, especially of the cartilaginous kind, in which it is very small in quantity, accompanied by a proportionally diminutive heart, and poor in red particles! the blood of the *Squalus Acanthias* I have found to exceed in density only a little its serum, one being of the specific gravity 1·030, the other of the specific gravity 1·027.

Whether the peculiar constitution of the red particles operates in any way in promoting their union with oxygen, seems to be deserving of consideration. It may be thrown out as a conjecture, that the circumstance of their possessing nuclei may

have an effect of the kind, supposing, which is possible, the blood-corpuscle and nucleus, or containing and contained part, to be in the electrical relation to each other of positive and negative. If it be objected to this, that as regards nuclei as well as size, there is an analogy between the blood-corpuscle of fishes, birds and reptiles, the temperature of which commonly is so very different, it may be answered, that in all these classes such a constitution of blood-corpuscle may be designed for the same end, and that birds partly owe their high temperature to it; and that in reptiles and fishes, in most of which the proportion of red particles is small, were the constitution of blood-corpuscle different, it would be inadequate to perform the part required of it.

II. *On the Temperature of Man in advanced age.*

Not aware of any observations having been published on the temperature of man in advanced old age, I have been induced to institute some trials, the results of which I shall now briefly describe.

1. 91 years of age; feeble on his legs, but in pretty good health; a native of Grasmere in Westmoreland, where he has always resided, in easy circumstances, cultivating his own land. In June, when the temperature of the air was 60°, a thermometer placed under the tongue rose to 99°·5; his hands were warm; his pulse at the wrist 48, strong, intermitting. The observation was made at 2 P.M.; he had dined at noon. On the 28th of the October following, his temperature was again tried, about the same time of day, when the open air was 42°, the air of his room 52°; now, under the tongue, the thermometer was 98°·5; the pulse 56; his state of health much the same as before.

2. 88 years of age, also a native of Grasmere, where he has mostly resided, as a day labourer; is pretty firm on his feet, but troubled with chronic cough and difficulty of breathing. In June, when the temperature of the air was 60°, a thermometer placed under the tongue rose to 99°·5; his pulse was 56, and rather feeble; he had dined three hours previously. On the 28th of October, an hour after dinner, when his pulse was 70, the thermometer under the tongue was 98°; the air of the room 55°. In February, about three hours after dinner, when his pulse was 44 and feeble, the temperature under the tongue was 96°. This was on the 27th, the air then of his room was 44°; the open air about 32°, after a heavy fall of snow, and a sharp frost of several days' duration. The old man was feebler than in the summer and autumn; and though he did not complain of cold, his hand felt cold.

3. The wife of the preceding, the mother of several children, 76 years of age; hale for her years, but blind from cataract complicated with amaurosis. Her temperature, tried at the same time as her husband's, in June, was found under the tongue to be 98°·5, her pulse 78, and pretty strong. Tried again in October, it was found to be 98°, with a pulse of 70; and again in February, on the 27th, it was found to be 99°; her pulse being 80.

4. 87 years of age, a native of Ambleside, where she has commonly resided; feeble, but, excepting chronic cough, in tolerable health. On the 26th of October, at 3 P.M., the temperature under the tongue was found to be 98°·5; her pulse 84, and pretty strong; the air of the room then was 57°, the open air about 42°.

5. On the same day, and in the same village, tried the temperature of another old inhabitant, 92 years of age. The thermometer under her tongue stood about 98°; it could not be determined with perfect exactness, on account of the tremulous motion of her head, which also affected the limbs, preventing the counting of her pulse; her general health was pretty good.

6. An inhabitant of Ambleside, by trade a hatter, 89 years of age, hale, able to walk to church. On the 27th of October, when the air of his room was 56°, the outer air 42°, his pulse 64, strong and regular; the thermometer under his tongue stood at 98°. Observed again on the 27th of February, at 1 P.M., just after dinner, when the outer air was 32°, the air of his room 54°, the temperature under his tongue was found to be 99°·5; his pulse 70.

7. The temperature of his wife, two years younger, taken on the 27th of October, was 98°·5; her pulse was 88, irregular; she was very infirm and suffering from asthma.

8. A native of Scotland, 95 years of age, now residing in Ambleside, where he has been many years, always in good health, still tolerably strong and active. On the 28th of October found his temperature under the tongue 98°·5; his pulse 56, intermitting; the air of his room 57°. The old people in all the preceding instances, at the time the observations were made, were sitting by their fireside, as is their usage in the cool climate of Westmoreland, the greater part of the year, and all of them, with one exception, seemed to be comfortably warm; the poorest of them were not in want.

Old age is commonly represented as cold, and the temperature of the body is commonly supposed to diminish with advancing age. The results of the preceding observations generally are not in accordance with this opinion; they seem on the contrary to show, that the temperature of old people, at least as regards the deep-seated parts, of which the tongue at its base may be considered as some indication, is rather above than below the average temperature of middle age, taking that to be about 98° of FAHR. Nor, perhaps, is this surprising, when we reflect, that most of the food consumed by old persons—and their appetite generally is good—is probably chiefly employed in administering to the function of respiration, being very partially expended in meeting the waste of the body.

Probably in very advanced old age, as in very early infancy, the power of resistance to cold is feeble, and the temperature of the body is easily reduced on exposure. An observation which I made many years ago in Ceylon would seem to be confirmatory of this. At 7 o'clock in the morning, when the air was 72°, I tried the temperature of an old man, almost a century old, and of a boy about twelve years old, both cool, being thinly clad and out of doors; the temperature of the old man under the tongue was 95°; in the axilla 93°; that of the boy under the former 98°, and in the

latter 96°·5. The observation too on the old man in Grasmere, made in February in cold weather, is also favourable to this conclusion: whilst those made at the same time, on the other two old persons in stronger health, seem to show, that, provided there is a vigorous action of the heart and free circulation of the blood, the temperature of the body is easily maintained.

III. *On the Effect of Air of different Temperatures on Animal Heat.*

As from observations made on man on entering the tropics, and within the tropics on descending from a cool mountainous district to a hot low country, it would appear that his temperature as measured by a thermometer placed under the tongue is liable to fluctuate,—rising one or two degrees in a warm atmosphere, and falling as much on entering a cool one*,—it seemed probable that like differences of effect might be produced by air kept at different degrees of temperature in buildings in this country.

In the autumn of last year, when going through the cotton manufactory of Deanstone, in the neighbourhood of Doune in Stirlingshire,—an establishment admirably conducted and in the highest order,—I availed myself of the opportunity to try the temperature of a few individuals in relation to this question. In the room called the "piecing-room," where a high temperature is always required on account of the kind of work,—a temperature kept up by means of warm air and steam,—when at 92°, I found the thermometer placed under the tongue of one man who had been at work there about six hours, rise to 100°·5; and of another, who had been there the same time, to 100°: the former was 52 years of age, healthy, his pulse 64; the other 33 years of age, in pretty good health, but liable to acidity of stomach; his pulse 78.

In an adjoining room, where the temperature of the air was 78°, the thermometer placed under the tongue of a young woman rose to 99°; and in a large room, where 300 persons were employed in weaving, and where the temperature of the air was 60°, the thermometer placed under the tongue of another healthy young woman rose only to 97°·5.

Few as are these observations, they seem to warrant the conclusion that a high temperature of even a few hours in the heated air of a room is capable of raising the temperature of the body above its usual standard, in accordance with what had been anticipated from the effect of different degrees of atmospheric temperature.

In further confirmation of the same, I may briefly state the results of multiplied observations made on the temperature of the same individual. The subject of them was of middle age, in good health, under whose tongue the thermometer commonly was stationary at 98°, when neither suffering from heat nor cold. The place where they were made was Constantinople,—the climate of which capital, it may be observed, is exceedingly variable,—often cold in winter and the early spring, and commonly very hot in summer,—liable to great vicissitudes from its situation on the

* *Op. cit.* i. 169.

confines of two seas, in regard to warmth very different in character during a great part of the year. The observations were begun early in March, and were continued at intervals till the latter end of July. During this time the thermometer in the open air ranged from 31° to 94°, and the temperature observed under the tongue from 97° to 99°·5. It may not be amiss to mention some particular instances.

On the 5th of March, after having been exposed several hours in an open boat on the Bosphorus, with a strong wind at 43°, the thermometer placed under the tongue stood at 97°.

On the 11th of the same month, when the ground was covered deeply with snow, and the thermometer in the open air at 7 A.M. was 31°, and in a bed-room 45°, the temperature under the tongue was found to be 97°·5.

On the 3rd of April, when the thermometer in the room, with the window open, was 66°, under the tongue it was 98°·5.

On the 17th of July, when the thermometer was 87°, under the tongue it rose to 99°·5. On the 21st of the same month, when the air was 87°, the temperature under the tongue was 99°·5; and on the 28th, when the former was 94°, the latter was 99°.

During the hot weather of July, it may be deserving of remark, that the pulse was less affected than the respiration, which habitually about sixteen in the minute, was now commonly fourteen, and one day did not exceed twelve.

It may also be mentioned that attention was paid to the temperature of the extremities, and also to that of the urine, and that commonly it was found of highest temperature when the tongue and extremities were of lowest temperature: thus, on the 5th of March, when the thermometer under the tongue was 97°, the feet and hands cold, in the urine it rose to 101°; and on the 28th of July, when under the former it was 99°·5, in the latter it was the same.

Do not these observations, besides tending to confirm the preceding conclusion for which they were brought forward, viz. that the temperature of the body rises and falls in a perceptible manner with the temperature of the air, lead also to the further conclusion, that the tendency of a high temperature of atmosphere is to raise the temperature of the surface and of the parts adjoining the surface in a somewhat higher ratio than the deep-seated organs; and of a low temperature of atmosphere to raise the temperature of the deep-seated parts, whilst that of the surface is subjected to undue reduction from the cooling agencies to which it is exposed, directed, as it were, in both instances, for a beneficial result, on the principle of compensation?

IV. *On the Effect of Exercise on the Temperature of the Body.*

This subject of inquiry, notwithstanding its manifest importance, has been much neglected; indeed, I do not know of any work in which any precise information is to be obtained respecting it.

The observations which I have to offer are fewer than I could wish and more limited; they were made at Constantinople in 1841, at intervals between February

and August, and had for their object mainly to endeavour to determine the effect of moderate exercise in walking on the temperature of the body. The individual on whom they were made was the same as was mentioned in the last section. The particular observations are the following:

February 19th, at 1½ P.M., air of room 60°; before walking, feet cold, temperature between the toes 66°; under the tongue 98°; urine 100°. At 5½ P.M., open air 40°; just returned from a walk, gently warmed by the exercise; feet and hands warm; the former 96°·5, the latter 97°; under the tongue 98°; urine 101°.

March 2nd, at 4½ P.M., open air 50°; air of room 66°; feet and hands moderately warm; the former 75°, the latter 81°; under the tongue 98°; urine 100°. At 5½ P.M., after having walked pretty quickly an hour, a gentle perspiration produced, the hands and feet hot, found the latter 99°, the former 98°; under the tongue 98°; the urine 101°·5.

March 20th, at 5½ P.M., open air 42°; returned warm after a walk of three hours: the hands, which had worn warm gloves, were 99°; feet 97°; under the tongue 98°; the urine 101°·5.

April 7th, after a walk of three hours in the open air, between 60° and 70°, returned at 5 P.M., gently perspiring: the hands were 94°; the feet 96°·5; under the tongue 98°·5; the urine 100°·5.

May 27th, at 6½ P.M., after a walk of an hour and half, the air 68°, returned slightly perspiring; the hands were 95°; the feet hot; under the tongue 99°·5; the urine 101°·5.

May 28th, air 65°; under the tongue before taking exercise 98°·5: after a walk of four hours and half, gently perspiring, under the tongue 98°; hands 93°; feet 97°·5; urine 100°·5.

September 13, at 4 P.M., the open air on the shore of the Bosphorus 76°: ascended in about twenty minutes, without stopping, the steep side of the hill, called the Giant's Mountain; on reaching its summit, when profusely perspiring, the pulse was 102°, usually about 52°; the hand 98°; under the tongue 98°. The pulse of another individual in company, of about the same age, also profusely perspiring, was 138°; thermometer under his tongue 98°; and in the hand the same. After descent, the pulse of the former was 94°; thermometer under his tongue and in the hand 98°·5; the pulse of the latter was 112°; the thermometer under his tongue 98°·5; both only gently perspiring.

What is the inference from these observations? Do they not seem to indicate that whilst moderate exercise promotes the diffusion of temperature and its exaltation in the extremities, it augments very little, if at all, the heat of the deep-seated parts? And considering the blood as the heating medium, warmed itself chiefly by respiration, is not this what might be expected, reasoning on the subject? By active exercise, the pulse and the respiration are both accelerated; more oxygen, it may be presumed, is consumed, more heat is generated; the blood is made to circulate more rapidly,

and is sent in larger quantity into the extremities, and where, in consequence, the excess of heat is conveyed and expended, and its accumulation in the central and deep-seated organs prevented, affording another striking example of harmonious adaptation.

The same thermometer was employed in making all the observations described in this paper; and in every instance, in stating the results, allowance has been made for error in its graduation, carefully determined by comparison with a standard instrument, one belonging to Professor Forbes of Edinburgh, and for the use of which I have been indebted to his kindness.

The Oaks, Ambleside,
Nov. 1st, 1843.

VI. *A Description of certain Belemnites, preserved, with a great proportion of their soft parts, in the Oxford Clay, at Christian-Malford, Wilts.* By Richard Owen, *Esq., F.R.S., &c.*

Received March 14,—Read March 21, 1844.

THE extinct Cephalopod, called *Belemnite*, has long been known by its peculiarly complex shell, which includes a part possessing the chambered and siphonated structure characteristic of the entire shell of the *Spirula* and *Nautilus*, and the fossil *Orthoceratites*, *Baculites*, *Ammonites*, &c. Like the latter unequivocal congeners of the still existing Nautilus, the Belemnites are distributed through a vast series of the secondary rocks from the epoch of the muschelkalk, when they seem first to have been introduced into the old ocean of this planet, up to the Maestricht chalk, when they finally perished.

No fossil shell has more exercised the ingenuity and research of the interpreters of ancient Nature, or has given rise to so many conflicting opinions as to the affinities of its animal constructor, than the Belemnite: but the specimens from the Oxford clay near Christian-Malford, in Wiltshire, liberally presented by the Marquis of Northampton, P.R.S., Samuel Peace Pratt, Esq., F.R.S., and William John Broderip, Esq., F.R.S., to the Royal College of Surgeons, leave no reasonable ground for further hesitation or scepticism on the subject, since they display in a truly marvellous manner, those soft and seemingly most perishable parts of the animal which are essential to convey a true idea of its living form.

It must, however, be premised in vindication of the fruitful principle of physiological correlations, established by Cuvier as the key to the interpretation of fossil remains, that, for some years prior to this discovery, there had been obtained sufficient evidence of the organization of the Belemnite, to determine both its ordinal and family affinities; but, as the value of this evidence failed to be appreciated by some experienced palæontologists, from want of sufficient knowledge of, or faith in, the laws of the interdependencies of the characteristic parts of the Cephalopodal organization, the additional facts afforded by the well-preserved specimens from the Oxford clay are most acceptable and valuable.

In the compound shell of these specimens the following parts are recognizable:—

1st. The terminal spathose body called the '*guard*,' sheath or rostrum*, resembling the head of a dart or javelin, whence the name Belemnite originally given to this part

* Plate II. fig. 1, *a*.

of the shell, which is usually the only part preserved, and now extended in its application to the entire animal.

2nd. The chambered or siphonated part of the shell which I have called the '*phragmocone**,' and which is lodged in the conical alveolus or cavity at the base of the 'guard.'

3rd. The conical, thin, but dense, corneo-nacreous case†, which immediately invests the phragmocone, and lines the alveolus of the guard; commencing at the bottom or apex of that cavity, and continued beyond the thin margins of the basal aperture of the alveolus, and beyond the last septum of the phragmocone, to form, as Dr. Buckland rightly describes‡, the large anterior chamber of the Belemnite containing the ink-bag and some other viscera.

The numerous species of Belemnite have been classified according to the modifications of the spathose guard; the one under consideration belongs to the group characterized by a rounded, elongated, conical guard, with a short, terminal, ventral, longitudinal impression; it was first recognised as a new species by Mr. Pratt, who has honoured me by naming it *Belemnites Owenii*. This species approximates in its general form to the *Belemnites elongatus* and *Bel. longissimus* of Miller, from the lias; but it presents intermediate proportions of length to breadth, and maintains the same diameter throughout a much greater part of its extent; the anterior expansion, which is very gradual, commencing, nevertheless, nearer the alveolar extremity, and ending less widely. The excavated part of the guard becomes very thin as it expands, and, there having been no infiltration of mineral matter into its cavity, or into the chambers of the phragmocone, it has yielded to the pressure of the superincumbent strata, and thus in its flattened and fractured state shows a greater degree of expansion than is natural to it. The thin and brittle margin of the spathose alveolus may be traced nearly half way towards the base of the phragmocone, which is there invested only by the thinner and more yielding corneo-nacreous sheath§.

The gradual expansion of the guard from its posterior end or apex is shown in the figure 1. The ventral groove (fig. 2 *a'*) extends to about one-fourth the length of the guard, commencing a little in advance of the apex: it is very shallow, with the

* Pl. II. figs. 1 *c*, 6, 7 and 8. Φραγμὸς partition, κῶνος cone. Lectures on Comparative Anatomy, 8vo, 1843, p. 333. The term 'alveolus' has usually been applied to the chambered cone; but it appears better to restrict it to the socket in which the chambered cone is lodged.

† Pl. II. fig. 6, and fig. 7, *y*. ‡ Bridgewater Treatise, 1836, p. 372.

§ In the specimen of *Belemnites elongatus* figured by Miller (Geol. Trans. 1826, Pl. VII. fig. 6.), this thin sheath, which extends beyond the wider part of the alveolus, had perished, as is usually the case, and the casts of the chambers of the phragmocone, which is preserved *in situ*, are exposed. To this is due the appearance which M. De Blainville was unable to understand in the figure above cited. "Ce que je ne conçois pas dans cette figure, c'est la manière dont les calottes empilées, qui constituent l'alvéole, dépassent de beaucoup la cavité de la coquille ou du tube, dont les bords sont cependant assez amincis pour croire que le péristome est parfait."—*Sur les Belemnites*, p. 95, 4to, 1827.

bottom not rounded, but defined by two parallel lines. The posterior half of the guard is slightly compressed laterally, and a very faint trace of a longitudinal impression may be discovered on each side, rather nearer the ventral than the dorsal surface. One of the specimens of the *Belemnites Owenii*, presented to the College of Surgeons by Mr. Broderip, measures eleven inches from the apex of the guard to the basal partition of the phragmocone: the diameter or breadth of that partition is one inch and a half: the length of the guard from its apex to the beginning of the crushed alveolus is six inches: the length of the ventral groove is one inch and a half.

With respect to the guard, I have little to add to the excellent descriptions of former authors, besides an account of its microscopic structure*: but this is the more requisite, as in some recent and estimable works the spathose structure is still regarded as the result of accidental posthumous infiltration. The guard consists of numerous, thin, for the most part concentric, layers† of minute prismatic trihedral fibres‡, placed at right angles, or nearly so, to the planes of the layers: the crystalline fibres are indicated by lines which radiate from the central axis and cross the lines of growth: the lines which define the fibres, when magnified 150 diameters, are seen in many parts of the section to run in pairs with a minutely and gently undulating course, resembling the tubes of dentine, but differing in the transparency of the intercepted calcareous matter, which is like that in the wider spaces separating the pairs of lines.

These differences in the intervals of the radiating fibres may depend on the different parts of the prismatic fibres divided in preparing the sections made parallel to their course.

There is an appearance not uncommon in microscopic sections of the spathose guard, which, though due to minute splintering or abrasion of the surface, is too characteristic of the texture of the guard to be passed over; it is produced by a number of elongated triangular specks§, defined by their opacity when the section is viewed by transmitted light, and by their white or silvery surface when viewed by

* This was first noticed by Dr. Carpenter in his valuable paper 'On the Microscopical Structure of Shells,' in the following words:—"The solid conical sheath of the Belemnite is a very favourable subject for microscopic examination; and of this I have made numerous sections. The greater part of these appear to have almost completely lost any indications of organic structure they may have once presented, being almost or completely homogeneous in their aspect. In some, however, I have met with a structure, which so closely resembles that of the massive *Septaria gigantea*, that I have no hesitation in the belief, that the shell of the latter is the nearest living analogue of the sheath of the Belemnite. I consider the term 'fibro-calcareous,' applied to the latter by Dr. Buckland, to be therefore erroneous; the structure being referable to the general type of membranous shells. The membrane seems to have been corrugated in a radiating direction, and as the deposition of calcareous matter followed the same, an appearance of radiating fibrous structure is given on fracture, which exactly corresponds with that of *Septaria*. The only difference between the two cases seems to have been, that, in the Belemnite the deposit took place from within outwards, whilst in the Septaria it was from without inwards."—*Extract from a Paper on the Microscopical Structure of Shells, by* William B. Carpenter, *M.D. Read to the Royal Society, December* 22, 1842.

† Pl. VII. fig. 1, β. ‡ Ib. fig. 1, γ; fig. 2, δ. § Ib. fig. 1, ε.

reflected light: the long axis of these triangles is always parallel to the fibres, and transverse to the layers; but on one side of the section the apices are turned towards the centre, on the other side towards the circumference of the guard; so that a slight change of focus reverses the position of the triangular specks.

The lines produced by the concentric layers of growth are seldom marked with equal distinctness; the strongest ones are usually in groups of three, five, or eight, with fainter lines in the clearer interspaces: this appears due to the varying thickness of the animal membrane at the contiguous surfaces of the layers of the prismatic fibres, which membrane was either formed by, or afforded attachment to the extremities of the delicate membranous cells which served as moulds for the calcareous matter of the fibres. The impress of these extremities has produced on many of the lines of growth a minutely undulating or crenate course. The layers of growth vary slightly in thickness; many are brought into view by applying a magnifying power of 150 diameters to a transparent section of the guard which otherwise would escape notice; those only being visible to the naked eye that are separated by the thicker lines; they are thus seen to be much more numerous than the septa of the phragmocone. In a transverse section through the middle of the alveolus, eighty layers could be counted in a thickness of a line, and more than three hundred in the solid part of a guard whose semidiameter was four lines.

A longitudinal section of the guard through its centre, and a transverse one, both demonstrate the longitudinal course of the radiating fibres, the linear indications of which might be interpreted as the folds of a plicated membrane: a longitudinal section taken near the circumference of the guard cuts across the radiating fibres, the extremities of which are thus seen in transverse section; their distinct and independent character and trihedral form are then clearly demonstrated, as in Pl. VII. fig. 2: they vary a little in size, the average diameter being $\frac{1}{1000}$th of an inch.

Through a great part of the thickness of the guard next the outer surface, the thin fibrous conical layers are concentric, progressively increasing in length as they approach that surface, and thus forming the alveolus or cavity for the phragmocone. The innermost or first-formed layers are not parallel with the outer ones, but recede from them at their anterior end, contracting as at the opposite end, but in a less degree, so as to form a slender cylindrical stem, sometimes slightly dilated at the end which is in contact with the apex of the capsule of the phragmocone. The interspaces thus left between the earlier and the later layers of the guard are occupied by more abundant animal membrane, mixed with coarser opake calcareous particles, like those which harden and render brittle the corneo-nacreous capsule of the chambers; a filamentary tract of the same kind of matter is continued from the apex of the above capsule down the centre of the guard to its posterior apex.

Mr. Pratt has obtained from the Oxford clay at Christian-Malford the guard of a young Belemnite, three lines long*, fusiform, slightly contracted posteriorly;

* Pl. II. fig. 4.

this must have belonged to an animal just excluded from the egg, if excluded at all. The layers of growth immediately added to this axis extend beyond it, both anteriorly and posteriorly; and, being thicker in the middle than at the two extremities, render the guard fusiform, as in the young specimen rather more than an inch in length* from the same stratum and locality as the preceding. At this stage of growth, which lasts longer in some species, as the *Belemnites subfusiformis*, than in others, the spathose guard has been mistaken for the spine of an Echinus, and this idea, first entertained of Belemnites in general by Klein, has been reproduced in later times by M. Raspail: even the sagacious Mr. Miller†, who has done so much towards the elucidation of the Belemnites, was led to conceive the fusiform guard of immature individuals to be remains of a distinct genus, for which he proposed the name of *Actinocamax*‡.

The exterior surface of the spathose guard of the Belemnites of the Oxford clay, though smoother than in some other species, is minutely granular, and occasionally presents faint traces of vascular impressions, proving it to have been invested by an organized membrane of the living Cephalopod. On two specimens from this conservative stratum, I have detected remains of a more immediate investment of a thin friable layer of white calcareous matter, analogous to that of the outer layer of the sheath of the phragmocone. The animal membrane or constituent of the spathose guard has been alluded to by Dr. Buckland as being evidenced by the odour resembling burnt horn, produced on burning this part of the Belemnite. I will only add in reference to the spathose calcareous constituent, that its microscopic structure proves it to be an original formation, deposited in membranous cellular moulds, under the influence of the vital organizing forces, and not to be the result of post-mortem infiltration of mineral substance, into an originally light and porous, or cellular texture, as Walch, Parkinson, Lamarck and De Blainville§ have conjectured.

As respects the phragmocone and its investing sheath, the well-preserved Belemnites of the Oxford clay demonstrate that the sheath is continued backwards to line the alveolar cavity of the spathose guard, as well as forwards from its basal outlet to form the visceral chamber anterior to the phragmocone. The phragmocone in these specimens appears broader than it actually was on account of the compression

* Pl. II. fig. 5.

† His conjectural figure of the recent Belemnite (Geological Transactions, new Series, vol. ii. (1826) Pl. IX. fig. 15) is essentially the same with those which have been since published by Dr. Buckland, M. D'Orbigny and M. Duval-Jouve.

‡ M. Duval (Mém. sur les Belemnites, 4to, 1841, p. 68) has demonstrated, what MM. De Blainville and D'Orbigny suspected to be, the true nature of the *Actinocamax* of Miller.

§ Sur les Belemnites, 4to, 1827, pp. 32, 33. Specimens of the spathose guard have been discovered which have been fractured during the life-time of the Belemnite, and healed; the broken portions having been held together by the surrounding organized integuments, and reunited by the deposition of new layers of the fibrous structure peculiar to the guard. Duval-Jouve, Sur les Belemnites, p. 37, Pl. X.

which its frail walls have been unable to resist; its basal part is usually squeezed flat, but sometimes one of the septa has slipped forwards so as to present its surfaces to the planes of pressure, and so retain its original form: one of these, which shows likewise its natural slight concavity, demonstrates the marginal position of the siphon as in other Belemnites, Pl. II. figs. 3 and 7, *i*.

The septa are composed chiefly of nacre with a thinner layer of white friable calcareous matter on both surfaces, which is seldom preserved. I have found twenty septa in an extent of two inches from the base of the phragmocone; about an equal number of septa dividing chambers progressively diminishing in depth, and more rapidly in width, are indicated, by detached phragmocones, to have extended to the apex of the socket of the guard. The capsule of the phragmocone consists of a thin layer of mixed albuminous and opake calcareous matter, lined with nacre, but with a yellowish smooth outer surface. In Lord NORTHAMPTON's well-preserved specimen, it terminates by a well-defined margin a little in advance of the ink-bag, forming there the true peristome of the shell, as shown in fig. 9.

The entire phragmocone, with its capsule, of these Belemnites from the Oxford clay, has been found not unfrequently isolated and detached, having slipt out of the alveolar cavity of the guard; such specimens are squeezed flatter than those which have remained in and been protected by the guard. The yielding texture of the phragmoconic capsule has commonly caused it to fall into longitudinal folds when compressed, after having become detached from the alveolus. In two specimens in the collection of Mr. CUNNINGTON of Devizes these folds are well-marked, regular, and on the same side of the capsule, forming two longitudinal grooves* in one and three in the other, the intermediate risings being so well defined as to appear like a structure original and natural to the capsule; but their position is different, and the degree of the indentation varies, and in other specimens the partial longitudinal impressions are barely discernible. If the change of form caused by the compression were not borne in mind, these piles of concave plates would seem not to have been adapted to the alveolus, and might thus be made occasions for the revival of the exploded idea of DE MONTFORT, that the phragmocone of the Belemnite belonged to an animal generically distinct from that which had constructed the spathose guard.

Belemnites whose remains have been left in strata percolated by streams containing mineral matter in solution, have the chambers of the phragmocone filled with crystals consequent upon such calcareous or siliceous infiltration: in the present Belemnites from the Oxford clay, no such infiltration has taken place subsequent to interment; we find only the delicate original calcareous framework of the phragmocone, crushed and squeezed out of its original shape, whilst the solid part of the spathose guard, by virtue of its proper primitive fibrous structure, has retained its cylindrical figure. This fact, independently of the microscopic evidence of organiza-

* Pl. II. fig. 6, *g*.

tion, suffices to prove that the weight and solidity of the guard had received no augmentation by inorganic influences after death*.

That the shell of the Belemnite was due to the formative forces of the mantle of a molluscous animal, was the sound speculation as to its nature, which our countryman Joshua Platt first recorded in the Transactions of the Royal Society for 1764. The presence of a camerated and siphonated structure in this complicated shell, led Walch† and Guettard‡, and after them most subsequent conchologists, to class the Belemnites with the Baculites, Orthoceratites, and other more simple chambered shells. Mr. Miller, having detected evidence of the internal position of the belemnitic shell, compared it, as Deluc§ on other grounds had done, with the internal shell of the Cuttle-fish, and first ventured on a conjectural restoration of the entire animal. He thought the Belemnite to have been an intermediate form in the Cephalopodal class, uniting the internal multilocular shell of the *Spirula* with the laminated calcareous plate of the *Sepia*, to which the belemnitic guard appears to correspond; and, believing that the *Nautilus*, *Ammonite*, *Sepia* and *Loligo*, had the same organization (only the *Dibranchiate* type of Cephalopodal structure being then known), Mr. Miller placed the belemnitic shell in the body of a Calamary (*Loligo*), assigning to the terminal fins the office of clasping the guard and retaining it in its proper position; which last idea M. De Blainville very justly rejected.

The subsequent discovery of two grades of organization in the class of Cephalopods, consequent on the dissection of the *Nautilus Pompilius*‖, called for a closer investigation of the affinities of the Belemnites, and led to an attempt to establish a more definite approximation of these with the other families of siphoniferous Cephalopods, now ranked under two distinct orders of the class.

The first evidence that bore directly upon the question of the position of the Belemnite in this class, was detected by Dr. Buckland¶ and M. Agassiz** in specimens of Belemnite from the lias at Lyme Regis, in which the fossil ink-bag was preserved in the basal chamber of the phragmocone, or that formed by the anterior prolongation and expansion of its capsule.

The importance of this discovery depends chiefly on the facts, that the secreting gland and reservoir of the inky secretion common to all the naked Cephalopods do not exist in the recent *Nautilus Pompilius*, and that no trace of them has ever been

* Such was Mr. Miller's opinion; but, as it was unsupported by microscopic investigation, or by any facts like that above cited, it was not accepted by Prof. De Blainville and Dr. Buckland.

† In Knorr's 'Recueil de Monumens des Catastrophes que le Globe de la Terre a essuyées,' &c. fol. 1768.

‡ Mémoires sur différentes parties des Sciences et des Arts, t. v. 9e Mémoire, 1783.

§ Mémoires sur les Bélemnites, in Journal de Physique, 1799, 1801, 1802.

‖ Owen, Memoir on the Pearly Nautilus, 4to, 1832.

¶ Philosophical Magazine, N.S. 1829, p. 388. [One of the specimens discovered by Miss Mary Anning of Lyme, on which Dr. Buckland's observations were made, has been presented, since the reading of the present memoir, by the Earl of Enniskillen to the College of Surgeons.]

** Ibid. 1834.

met with in connection with any of the simple or typical forms of fossil chambered shells, as the *Orthoceratites*, *Baculites*, *Ammonites*, &c.

Reflecting on this marked difference in the anatomy of the Nautilus, I was led to perceive that, as this rare Cephalopod derived sufficient protection from its large and strong external shell, it might well dispense with that peculiar glandular apparatus which had before been deemed a common character of the Cephalopodal class; whilst on the other hand, as the highly organized naked Cephalopods enjoy active powers of locomotion which would be incompatible with the incumbrance of a heavy external testaceous defensive covering, they required a compensatory endowment of the power of secreting an inky fluid, which, when alarmed, they might inject into the surrounding water and conceal themselves by the dusky cloud thus occasioned. But the branchial character of the naked order of Cephalopods is an essential condition of their muscular powers; the presence of an ink-bladder, therefore, in the extinct Belemnites, would have implied the internal position of the shell, even if other proof had been wanting; and, by the laws of correlation, it implies likewise the presence of the muscular forces for rapid swimming, and the concomitant conditions of the respiratory, the vascular and the nervous systems. Connecting, therefore, all these considerations with the detection of the ink-bag in the shell of the Belemnite, I felt justified in referring the Belemnites, and likewise the Spirula, on account of the ascertained internal position of its shell, to the Dibranchiate order; and I therefore separated these chambered and siphoniferous shells from the Nautilus and the Ammonites, in the classification of the *Cephalopoda* submitted to the Zoological Society in February 1836*.

But the true grounds of this separation seem not to have been appreciated or understood by some Palæontologists. Professor Phillips, for example, in his excellent article on *Turrilites*, in the part of the Penny Cyclopædia published in January 1843, has observed, "The relations of Turrilites, Scaphites, Baculites and Hamites to Am-

* Zoological Transactions, ii. pp. 127, 129. "The *Cephalopods* with internal chambered shells, heretofore classed with the *siphoniferous Cephalopods*, which constitute the preceding order, I would join with all the other *naked Cephalopods*, to form a second order, under the term *Dibranchiata*, having reference to the number of gills, viz. two. This number is constant in all the '*Seiches*' of Cuvier, and is associated with the presence of two branchial hearts, besides the single systemic heart, and with an ink-bag; there can be little doubt that the same type of structure is exemplified in the *Spirula*, from what has been determined respecting its external characters[3]." [3] "The discovery by Dr. Buckland of the remains of the ink-bag in the extinct *Belemnites*, justifies the conclusion from the laws of coexistence, that these *Cephalopods* also possessed two gills and two branchial hearts." In the same year, 1836, the Number of the Cyclopædia of Anatomy and Physiology was published, containing my Article '*Cephalopoda*,' in which it is argued of the *Belemnites*:—"As it is certain that the animals of this family of extinct *Cephalopods* possessed the ink-bag, they must consequently have been enveloped by a muscular mantle; and we may, therefore, infer that they resembled the *Dibranchiates* in their locomotive and respiratory organs, and consequently in the general plan of their organization. In the structure and position of their siphoniferous camerated shell, they are intermediate to *Spirula* and *Sepia*, and as the animal of *Spirula* is proved to be a *Decapod*, the probability is very strong that the animal of the *Belemnite* was of the same type."—p. 520.

monites is very obvious; and, as through Goniatites, this great extinct group is certainly connected to the living and extinct *Nautili*, Mr. Owen has ventured to include them all in the Tetrabranchiate Cephalopoda, leaving Spirula and the Belemnites with Sepia and the Dibranchiate types. However this may be, the determination of the relative affinities among the numerous fossil Cephalopods, a point of great importance, must be worked out with the help of other considerations than the respiratory system." In the memoir on the 'Classification of *Cephalopoda*,' above cited, it will be found that many other considerations than those of the respiratory system, and of equal importance with them, influenced me in forming an opinion of the natural position of the Belemnites in the class *Cephalopoda*.

Leopold Von Buch, who believed that he could trace in certain slabs containing Belemnites the impressions of the Cephalopods to which they belonged, concluded "that the body of the animal enveloped the greater part of the shell, and exceeded its length by eight or ten times*." Other considerations taken from the shell itself prove, as has already been shown, that it was wholly internal.

The specimen† presented to the Hunterian Museum by the Marquess of Northampton, exhibits the phragmocone, the muscular mantle, a small part of the head, and a greater or less proportion of six of the cephalic tentacula which are armed with horny hooks in a double alternate series, as in the *Onychoteuthis gigas*.

The phragmocone with the soft parts of the Belemnite has been detached from the guard probably soon after death; and the whole squeezed nearly flat after becoming interred in the laminated clayey matrix. The resistance of the ink-bag (*n*) with its inspissated and indurated contents, has led to abrasion and loss of the walls of the part of the phragmocone covering it, and it seems to have been pressed downwards through one or two of the basal partitions deeper into the sheath than was natural, or than it is situated in other specimens. The capsule of the phragmocone extends about one-third of an inch beyond the ink-bag, and terminates by a well-defined border. The smooth surface of its opake white external calcareous layer is well preserved over nearly the whole of this part. The muscular tunic of the mantle (*d*) appears to commence at the peristome; it seems to have first undergone the change into adipocire and then to have become so brittle as to crack and break instead of bending to the pressure; the course of the muscular fibres is plainly visible; all those on the outer surface of the mantle which is presented to the observer, are transverse or circular; this surface is smooth, and the course of the fibres more feebly indicated; in the few places where the upper side of the mantle is broken away, and the inner surface of the opposite side shown, the arrangement of the transverse fasciculi is more strongly displayed.

In the length as compared with the breadth of the mantle, the Belemnite is shown by this beautiful specimen to have had the same elongated form of body as the *Onychoteuthis* and most modern *Decapoda*.

* Oken's Isis, Bd. xxi. p. 438. † Pl. III.

A little above the capsule of the phragmocone, on the left side, there is a flattened transversely fibrous body (*e*) with a rounded external border, so well defined as to excite the suspicion that it must have belonged to some part superadded to the muscular mantle; its nature is demonstrated in the specimen next to be described.

An oblong portion of the same fibrous and muscular tissue as the mantle, lying obliquely in front of the anterior margin of the mantle, and in which both a longitudinal and transverse layer of fibres are discernible, seems to be the remains of the infundibulum or expiratory tube (*f*).

The direction of the fibres in the cephalic arms is chiefly longitudinal; the magnified figure* precludes the necessity of describing the shape of the horny hooks; their arrangement in a double alternate series is manifested in some parts of the arms, but is still more obvious in the third specimen† to be described.

The second less complete but highly instructive specimen of the Belemnite‡ is from the collection of Mr. Pratt; it exhibits part of the muscular mantle (*d*), the two fins (*e*, *e*), apparently the infundibulum (*f*), the ink-bag and duct (*n*), and a considerable proportion of the phragmocone (*c*). This part is more distorted and less entire than in the preceding specimen, but, so far as a comparison can be made, presents the same form and structure§.

The reservoir of ink is situated two lines within the aperture of the phragmoconic capsule, which terminates with the same well-defined border; it is of an oval form and jet black colour, with a feeble indication of its original nacreous outer coating: the inspissated ink is very hard, brittle and splintering; when reduced to a fine powder it presents a dark brown hue, and, used as a pigment, works as smoothly as Roman Sepia, but with a deeper tint.

The Belemnitic ink-secretion offers the closest resemblance with that described by Dr. Buckland from the lias of Lyme Regis, and which he found associated with a series of circular transverse plates and narrow chambers, resembling the chambered cone within the alveolus of a Belemnite, and from which Dr. Buckland inferred that the animal, from which these fossil ink-bags were derived, was some unknown Cephalopod, nearly allied in its internal structure to the Belemnite, the circular form of the septa showing that they could not be referred to the molluscous inhabitant of any Nautilus or Ammonite‖.

The absence of the ink-apparatus in the Nautilus and allied extinct chambered Cephalopods adds demonstrative proof, were such required, of the accuracy of Dr. Buckland's negation, whilst the association of the spathose guards with crushed phragmocones, identical in structure with those in connection with the fossil ink-bag and muscular parts of the specimens under consideration, and all from the same

* Pl. IV. fig. 2. † Pl. V. ‡ Pl. IV. fig. 1.

§ Near the confused remains of the head in this specimen there is the impression of part of the phragmocone of another Belemnite.

‖ Philosophical Magazine, 1829.

stratum and restricted locality, admits of no reasonable doubt of their belonging to one and the same species of true Belemnite.

The two flattened fibrous bodies, (*e*,*e*) with well-defined semi-oval external and apparently free margins,—the one on the right side entire, the one on the left having the contour of the defective part of the margin indicated by the dark carbonaceous stain in the matrix,—are the parts which I regard as the lateral fins of the mantle. They have been slightly displaced transversely and pressed inwards upon the yielding viscera; their original cartilaginous basis would favour their encroaching in that direction if subjected to equable surrounding pressure: the lateral fin which is preserved in the first specimen* has been pushed more deeply inwards.

The large end of the semi-oval free border is the anterior one, where the fin is broadest; it gradually becomes narrower posteriorly. The muscular fasciculi are strongly marked, and are arranged transversely to the long axis of the fin, as in existing Decapodous Cephalopods. It is interesting to find a rounded contour associated with an advanced position of the lateral fins in the ancient Belemnites, as in the modern *Rossia* and *Sepiola*, the rhomboidal form being most common in those fins which are placed at the end of the body, as in the Onychoteuthis and Loligo; the only exception, indeed, being presented by the *Loligopsis*, which has terminal and rounded fins.

M. Duval, the latest and most accurate author on fossil Belemnites, reproduces† the figure which M. D'Orbigny has published, and which is essentially the same as that given by Dr. Buckland in his Bridgewater Treatise; and, like it, differs from Mr. Miller's restoration, in the position of the ink-bag and in the extended state of the terminal fins. With respect to these parts, M. Duval, from his discovery of the united fractures of the spathose guard, has objected with much acumen, that, if the fins of the Belemnite had been placed at the side of the guard, they must have been rendered useless by its fracture, and the creature, thus deprived of its power of swimming, would soon have fallen a prey to its numerous enemies, and would not have survived to exemplify the reparative powers of those ancient Cephalopods. M. Duval, however, modestly concludes by confessing that he should not have dared himself to figure from the known analogies, the animal to which the Belemnite ought to have belonged; for "I have not," he says, "a sufficiently exact knowledge of the organic laws of the Cephalopoda." It seemed vain to hope that the soundness of the principles on which the classification of the Belemnites with the dibranchiate Cephalopods had been definitely proposed, should ever be vindicated by the demonstration of parts, apparently so perishable as the fleshy mantle, the fins, and the slender flexile arms of these ancient Mollusca‡.

* Pl. III.

† Sur les Belemnites, 4to, Pl. 7. fig. 10.

‡ Cuvier, in the second edition of the 'Règne Animal,' places the *Belemnites* between the *Orthoceratites* and the *Ammonites*, and observes, "*ils appartiennent probablement encore à cette famille, mais il est impossible de s'en assurer, puisqu'on ne les trouve plus que parmi les fossiles*," tome iii. p. 19,—which teaches how liable the best authorities are to err, when they would set bounds to the possibilities in Nature.

But we derive from the present remarkable specimens ample confirmation of the association of the ink-bag with the higher grade of the circulating and respiratory organs, which grade is necessarily associated with the high development of the locomotive system, as demonstrated by the muscular mantle and its appended fins; whilst the preservation of the latter organs *in situ* establishes the soundness of M. Duval's objections to their position in all the published conjectural restorations of the Belemnite.

In the specimen under consideration* the fins are crossed by a narrow tract of grey transversely fibrous substance, probably part of the mantle, near the anterior termination of which an oblong flattened tract of similar substance extends forward, slightly expanding as it advances to a position opposite the neck of the Belemnite, where it is terminated by a slightly concave truncation: longitudinal fibres may be discovered decussating the more abundant transverse fibres of the part which is most probably the remains of the infundibulum. A short flattened band of fibres (*g*) connects this part with the neck of the Belemnite, having the exact position and proportion of the retractor or levator muscles of the infundibulum of the naked Cephalopods†. The traces of muscular tissue in the situation of the head are much more obscure: two short processes from the anterior part of this mass are evidently the bases of tentacula or cephalic arms.

At the middle of the visceral mass, in the interval of the two lateral fins, there lies a compressed body of a horny texture and sub-bilobed form (*m*), on which may be clearly distinguished striæ passing outwards in opposite directions from a middle line and diverging from each other in their course, which resembles that of the fibres of the digastric muscle in the gizzards of the Nautilus and other Cephalopods: this apparent remnant of the stomach lies about half an inch in advance of the ink-bladder, in a position corresponding with that of the gastric organ in naked Cephalopods.

There is strong negative evidence that the Belemnite possessed horny mandibles like the other naked Cephalopods, since no calcareous beaks, or Rhyncholites, have been discovered associated with the specimens from the Oxford clay, or with those from the lias.

The thickness of the layer of dried and compressed grey fibrous matter to which the mantle is reduced is half a line, and we may infer from this, that in its soft and recent state, when permeated by its sanguiferous vessels, it must have equalled in thickness that of a Calamary of the same size. In fact the mantle of true *Teuthidæ* (Calamaries with horny pens), preserved in the same matrix as the Belemnites here described, has been reduced to a compact fibrous layer of the same thinness: a specimen of one of these‡ displays by a fracture of the layer of the clay in which it was imbedded, the anterior and posterior walls with the intervening cavity of the abdomen, exposing the ink-bag and duct *in situ*.

* Pl. IV. fig. 1.

† Compare fig. 10, *g*, with Cuvier's Pl. 1. fig. 2, *m*, *n*, Mémoire sur le Poulpe, 4to.

‡ Pl. IV. fig. 2.

In neither of the above described specimens of Belemnite having the soft parts and phragmocone in natural connections, is there any evidence of the muscular part of the mantle having been continued over the capsule of the phragmocone; it is traceable for a short way below the peristome in Mr. CUNNINGTON's specimen*; but it is best developed where it surrounded the compressible part of the body of the Belemnite anterior to the shell. There seems no reason, however, to doubt that the skin, which, in existing naked Cephalopods is thin and lubricous, and more easily detached from the subjacent muscular layer than in the lower Mollusks, was extended over that part of the phragmocone extending beyond the alveolus, as there has been already shown evidence of its continuation over the alveolar and solid part of the spathose guard: its gelatinous base was less favourable for preservation than the fibrinous nature of the muscular tunic, and its destruction is, therefore, not surprising. The dark stain upon the clayey matrix, which usually extends a little beyond the preserved muscular structure, may in part be due to the pigmental cells of the skin; and these seem evidently to have produced the thin crust of a dark greenish colour which hides part of the fibrous layer of the mantle in the third specimen left for description.

This†, which is from the collection of Mr. PRATT, is chiefly remarkable and valuable for the perfect conservation of the complex muscular structures of the head and its uncinated arms. Eight of these, forming the normal series of cephalic arms, may be defined, radiating from a contracted base. In this base may be observed two decussating groups of curved fibres (*h*), the posterior one with its concavity turned towards the mantle, the anterior one with its concavity directed forwards, and its horns continued into the bases of the arms. A similar decussated arrangement of fibres exists in the *Onychoteuthis*, and is described and figured by CUVIER in the corresponding part of the head of the *Octopus*. Almost the entire extent of five of the cephalic arms is preserved, as shown in the figure; they are rather longer in comparison with the mantle than in the modern Onychoteuthis, but not as compared with the entire body of the Belemnite when this is lengthened out by the terminal spathose guard: the longitudinal arrangement of the fasciculi of muscular fibres of the arms is very distinct.

I placed a portion of the muscular tissue under the microscope, and succeeded by the aid of a drop of diluted acetic acid in softening and unravelling the constituent fibres‡; they presented the same size as the fibres from the corresponding part of one of the arms of an *Onychoteuthis*, but the faint transverse striæ visible in the recent fibre§ had disappeared in the fossil, and only an obscure granular structure could be discerned.

Each of the arms seems to have been provided with from fifteen to twenty pairs of hooks‖, which were doubtless developed from the horny hoops which encircled the caruncles of the acetabula, as in the modern *Onychoteuthis*.

* Pl. VI. fig. 1, *d*. † Pl. V. ‡ Pl. VII. fig. 4. § Ib. fig. 3.

‖ Pl. VI. fig. 2, is a magnified view of the most perfect of these hooks.

Two small protuberances at the origin of the normal brachia are the only parts which represent the bases of the pair of long tentacula, superadded to the eight shorter arms in the existing *Decapoda*.

On each side of the head, behind the bases of the arms, there is a convex protuberance formed by a well-defined semicircular band, about a line in thickness, of grey fibrous matter, the fibres or layers being parallel with the curve of the band. These parts are more distinctly shown in Mr. CUNNINGTON's specimen, in the description of which the reasons for regarding them as belonging to organs of vision are given. In the present specimen they indicate, according to this view of their nature, that the eye-balls of the Belemnite were sessile*, and agreed in size, as in position, with those of the modern naked Cephalopods.

Another specimen of similar size, in the collection of Mr. PRATT, exhibits the upper two-thirds of the visceral cavity formed by the mantle and the head with the bases of the arms, one of which is preserved to the extent of two inches, another to that of one inch, and on both these a few of the horny hooks remain. At the lower part of the head a circular amorphous granular mass is visible; it is bounded anteriorly by a curved fasciculus of fibres with the concavity directed backwards: above these the fibres which are continued into the bases of the arms commence from a fasciculus curving in a direction opposite to the preceding. These decussating bands are similar to those in the former specimen but are more strongly marked. The fibres continued into the arms are chiefly longitudinal. The few hooks which are preserved in this specimen are identical in size and shape with the more perfect series in the preceding specimen.

There is a minute trace on the left side, near the lower end of the specimen, of an obliquely striated horny plate. Most of the preserved fibrous structure of the flattened mantle is transversely arranged, as in all the other specimens; but a faint trace of longitudinal or retractile fibres may be discerned near the anterior margin of the mantle.

The fracture of the slabs of clay containing the last two instructive specimens has crossed obliquely that part of the abdomen in which is situated the striated thin horny plate, agreeing with that which I have ascribed to the gizzard: wanting therefore both the ink-bag and phragmocone, these specimens were defective in the requisite evidence to associate the uncinated arms with the complex shell, muscular mantle, and rounded fins of the Belemnites.

The coexistence with the true Belemnites, in the Oxford clay at Christian-Malford, of fossil Calamaries with a dorsal horny gladius or pen, like those from the lias at Lyme Regis described by Dr. BUCKLAND†, made it still more desirable to obtain such evidence as could only be given by more entire specimens of those ancient uncinated Cephalopods than those above described from the collection of Mr. PRATT, which were the first and for some time the only specimens of the kind that I had seen.

The subsequent fortunate discovery of the unique example‡ submitted to my ex-

* In the *Nautilus* the eyes are pedunculated. † Bridgewater Treatise, i. p. 308. ‡ Pl. III.

amination by the noble President gave the much-desired solution to the question; the form of the muscular part of the mantle, the proportions of the arms, and the number, shape and disposition of the horny hooks, being identical in that specimen of the Belemnite with those in the beautiful one with the crown of uncinated tentacles formerly in Mr. PRATT's cabinet, and now deposited, with the more perfect Belemnite from Lord NORTHAMPTON's collection, in the Hunterian Museum.

I have more lately been favoured by Mr. CUNNINGTON of Devizes with the temporary possession of the instructive specimen* of the *Belemnites Owenii* obtained from the same stratum and locality as the foregoing. It exhibits a considerable proportion of six of the cephalic arms; one of them is three inches and a half in length, but not entire; a full inch of another is indicated or represented by the double series of hooks, in their natural relative position, there being ten pairs in this extent.

The muscular tissue, forming the common base of the arms (*h*), has been preserved in a more compact mass than in Mr. PRATT's specimen, but the arrangement of the fibres is distinguishable. A median fine groove may be traced along each of the best preserved arms, indicating the cavity in which the artery and nerve were lodged.

From near the side of the common uniting base of the ordinary uncinated arms a long and narrow tract of fibrous matter (*k*) bends down along the side of the head to the beginning of the mantle, becomes more slender than the cephalic arms, and is reflected, with an irregular twist, forwards again; this is obviously the basal part of one of the long superadded tentacles.

The most marked and peculiar character of the present specimen is seen in the part of the head immediately behind the base of the arms; at this part, imbedded in the usual grey remains of the muscular tissue, are two semicircular portions of a denser and darker greyish brown fibrous substance (*l l*), obviously the same parts as those above described and referred to the eyes, in Mr. PRATT's second specimen†; the parts in question are regularly placed in reference to each other in the present specimen, being on the same transverse line, with their concavities towards each other, and their convexities turned outwards: each body is a line in breadth and does not diminish at either extremity, which is lost in or hidden by the surrounding muscular tissue: their structure is more minutely but more definitely fibrous than in the muscles, the fibres following the curve of the band. The parts in existing Cephalopods, which first suggest themselves for comparison with these, are, the beak, the cartilage of the head, the cornea or the crystalline lens. The position of the curved fibrous bodies is posterior to that in which the beak should be placed, agreeably with existing analogies; the texture of the beak, also, in the *Onychoteuthis* is the same as that of the hooks, whilst that of the parts in question is very different from the black horny matter of the preserved hooks. The position of the parts in the present specimen, like that in Mr. PRATT's, corresponds with that of the large sessile eyes, only that they

* Pl. VI. fig. 1. † Pl. V.

are more nearly approximated towards each other. In reference to the large crystalline lens which characterizes the eye in naked Cephalopods, the parts in question can only be compared, from their size, with the exterior laminæ of the outer division of the lens, in which case the larger and denser inner division of the lens has not at all been preserved; which is by no means a probable occurrence, and induces me to reject this analogy. If we compare them to the strong external tunic of the eye, their outward convexity would lead to their being referred to the cornea. But this part, in all existing Cephalopods is a modification of the integument, and continuous with it, presenting a less degree of convexity than in the fossils, less thickness, and a less definite extent. Viewing, however, the relative position, form and structure of the parts under consideration in the two specimens in which they are preserved, the most probable conclusion respecting their nature appears to me to be that which refers them to the anterior or external tunic of the eye-ball, in which case they indicate a thicker, stronger, more distinct, more extensive, and more convex cornea in the Belemnite than in any known existing Cephalopods.

Just behind the eyes is an oblong body in which a fine longitudinal arrangement of fibres is visible; this may be the remains of the funnel: in the adjoining part of the mantle the transverse fasciculi are, as in the other specimens, plainly discernible. The left fin (*e*) is well preserved, and the contour of part of the right fin, as it seems to me, is traceable, folded back upon the mantle. The left fin presents exactly the same relative size and semi-oval contour of the free margin which is shown in Mr. Pratt's specimen; it has been slightly displaced, and advanced obliquely near the anterior border of the mantle. A very compact shining dark-coloured substance at the detached basal margin of this fin may be the charred remains of its supporting cartilage. The right fin, the free border of which is bent inwards upon the mantle, as is not unusually seen in ordinary naked Cephalopods, has preserved its true position, rising a little above the visceral chamber of the phragmocone. The most important additional fact which we derive from the present specimen is the continuation of the mantle over the sheath of the phragmocone, proving indisputably the internal position of that part. The chambered division and thin calcareous and nacreous structure of the crushed remains of the phragmocone are quite identical with those of the phragmocones preserved with the spathose guard in the specimens from Mr. Pratt's and Mr. Broderip's cabinets.

In the present specimen about one inch of the apex of the phragmocone has been separated from the rest, but its impression is distinctly preserved: in this we may trace the longitudinal fold of the crushed capsule, and the impressions of the chambers and septa to within a few lines of the apex. At the anterior part of the phragmocone we have the depression in which the ink-bag with its indurated contents was lodged. Remains of a thin horny plate are situated anterior to the ink-bag.

The evidence afforded by the above-described specimens of the paucity in number and superiority in size and complication of the cephalic tentacles of the Belemnite,

as compared with those of the Nautilus, yields another proof of the constancy of the laws of organic correlation; the very numerous, small, and comparatively simple tentacula of the Nautilus, which illustrate the principle of vegetative or irrelative repetition, being associated with an essentially inferior type of Cephalopodal organization, into which an internal shell, a thick muscular mantle, pallial fins, and an ink-secreting apparatus do not enter.

The cephalic arms of the existing species of Onychoteuthis present at the present day the highest grade of organization that has been observed in these characteristic prehensile instruments of the Cephalopoda. The great specimen captured by Banks and Solander off Cape Horn in the first voyage of Captain Cook, offers the best example of this formidable prehensile structure, since, not only were the extremities of the two long tentacula beset with hooks, but all the eight normal arms supported a double alternate series of uncinated acetabula.

But in comparing the different forms of Cephalopods that have successively appeared and perished since the deposition of the lias to the present time, we do not find that the above most complex organization of the cephalic arms has been attained by or through progressive gradations, typified by the organization of intermediate forms: the ancient Belemnites manifested the uncinated armature as perfectly as the most formidable of existing *Onychoteuthides*. Nor were true Calamaries, with uncinated arms, absent in those primeval seas, which were tenanted by living Belemnites, Ammonites, and other extinct forms of Cephalopoda. The existence of naked Cephalopods of the family *Teuthidæ* in the oolitic secondary formations, has been for some years demonstrated by the well-preserved and recognizable remains of the ink-bag, the gladius or horny pen, and the horny hooks developed from the acetabula of the cephalic arms.

These singular fossils have been elucidated by the minute and accurate descriptions of Dr. Buckland*, and have elicited some beautiful remarks from the same eloquent writer in his Bridgewater Treatise†. They have been noticed and described by Zeiten, by V. Meyer, and Count Munster, from the lias schale of Aalen and Boll, and from the Solenhofen slate. The impression of an entire Onychoteuthis with the double series of hooks belonging to the eight short arms, nearly in their natural position, is figured in the Sixth Livraison of M. D'Orbigny's 'Paléontologie Française,' 8vo, now in course of publication, under the name of *Celæno speciosa*, assigned to it by Count Munster. These hooks very closely resemble those of the *Belemnites Owenii*, but their base is rather less recurved, and they are more closely arranged: the fleshy part of the arms is not preserved; but they were evidently shorter in proportion to the mantle than in the Belemnite.

In conclusion, if we compare the Belemnite as now restored‡, not conjecturally, but by observation of phenomena, with the known existing forms of the Dibranchiate

* Proceedings of the Geological Society, 1829. † Vol. i. p. 303. ‡ Pl. VIII.

or higher order of Cephalopods, in which its right of place can no longer be disputed, we shall first recognize in the outwardly concave plates and margino-ventral siphon of the chambered shell of the Spirula, the analogue of the hydrostatic part of the shell or phragmocone of the Belemnite: next in reference to the entire shell we must admit, agreeably with the opinion of De Luc, Miller, De Blainville and Buckland, that the *Sepia* or common Cuttle Fish, most nearly resembles the Belemnite in the general structure and position of its complex calcareous plate. The nucleus or terminal spine of the sepium or cuttle bone corresponds with the terminal spathose guard of the Belemnite; the convex posterior broad plate of horny with friable calcareous matter is analogous to the capsule of the phragmocone; but its margins, instead of being approximated and soldered together, are free and lateral in position: the congeries of transverse plates, lodged in the concavity of the nucleus and of the foregoing semi-capsule of the cuttle-bone, answer to the chambered phragmocone of the Belemnite, but, instead of being perforated by one or many siphons, they are entire and connected with each other by a series of minute undulating lamellæ perpendicular to their plane.

The lateral fins of the Sepia are narrow, and extend, as is well known, from the apex of the mantle to near its base; while the fins of the Belemnite were relatively shorter and broader, and situated a little in advance of the middle of the body. In the relative size, shape, and position of the fins, the Belemnite must have most nearly resembled the species of the existing genera *Rossia* and *Sepiola*, but it differed in the more elongated and slender body.

The character of the formidable hooks, supported by the acetabula of the arms, is now exclusively manifested by the genus *Onychoteuthis*.

Thus the extinct Belemnite combined characters at present divided amongst four distinct genera of Dibranchiate Cephalopods, *Spirula*, *Sepia*, *Sepiola*, and *Onychoteuthis*. But, notwithstanding the uncinated character of the arms, the balance of its natural affinities seems to me still to preponderate in favour of its position as a transitional link between *Spirula* and *Sepia*: and the additional facts which we have now unexpectedly gained, while they show new and unsuspected radiations of affinity tending to complete the reticular interdependencies of the Cephalopods, do not disturb, but confirm the position of the Belemnite, in the linear series of the genera of that class which I proposed in 1836.

The Belemnite, with the advantage of its dart-shaped and well-balanced shell, must have enjoyed the power of swimming backwards and forwards by the action of its cephalic and pallial fins, with greater vigour and precision than the modern Decapod *Dibranchiata*. The position of the animal was, most probably, more habitually vertical than that of its recent congeners. Thus placed, the Belemnite, in quest of prey, would rise swiftly or stealthily to infix its claws in the belly of a supernatant fish, and then dart down, and drag its prey to the bottom and devour it. And we

cannot doubt, but that, like the uncinated Calamaries of the present seas, the ancient Belemnites and their associates, the Celænos, were, in their day, the most formidable and predaceous of Cephalopods.

We admire the skill of the Egyptian embalmers, which has enabled Cuvier* to test the influence of time in transmuting specific forms, by a comparison of the *Ibis* of the present century with one that died 3000 years ago. The researches of the chemist may afford an insight into those properties of the soil, in which the above described valuable and instructive specimens of Cephalopoda were entombed, that favoured the apparent conversion of their muscular tissue into adipocire, and its subseqnent preservation to the present day. I can only describe this conservative matrix as a peculiarly fine and compact, but fissile, laminated variety of the Oxford clay: a formation at the base of the great middle oolitic system, more ancient than the Portland stone, the Wealden and the entire Cretaceous group. The Cephalopods in which we may now study the microscopic character of the muscular fibre, must therefore have existed at a period antecedent to the gradual deposition of these enormous masses of the secondary strata, which themselves preceded the formation of the entire tertiary series, and the overspreading unstratified masses, called diluvial. The attempt to conceive or calculate the period of time which must have elapsed since the Belemnites were thus embalmed, baffles and awes the imagination.

Description of the Plates.

All the figures are of the same species of Belemnite (*Bel. Owenii*, Pratt), and of the natural size, except where otherwise indicated.

The following letters indicate the same parts in each figure.

a. The guard.
b. The alveolus or socket of the guard for lodging,—
c. The phragmocone; ζ, the sheath; θ, septum; ι, siphon.
d. Muscular tunic of the mantle; η, fold of the sheath.
e. The pallial fins.
f. The infundibulum.
g. The levatores infundibuli.
h. Decussating muscular fibres of the head.
i. The uncinated arms.
k. The tentacula.
l. The eyes (?).
m. The lining or muscular tunic of the stomach.
n. The ink-bag.

* Discours Préliminaire sur les Révolutions du Globe, Ossemens Fossiles, tom. i. p. 141.

PLATE II.

Fig. 1. Spathose guard and crushed phragmocone of a *Belemnites Owenii*.

Fig. 2. Apical extremity of the guard, showing the ventral groove α, and the form of the transverse section above the groove.

Fig. 3. A transverse section of the guard through the alveolus, showing one of the partitions of the phragmocone.

Fig. 4. The guard of an embryo Belemnite.

Fig. 5. The guard of a young Belemnite, in the condition of an *Actinocamax*.

Fig. 6. A detached and crushed phragmocone, showing the folds of the capsule at η.

Fig. 7. A detached and crushed phragmocone in its capsule, η, with one of the partitions, slipped forwards, θ.

Fig. 8. A detached partition from near the base of the phragmocone.

PLATE III.

The specimen of *Belemnites Owenii*, from the Oxford clay, from the collection of the Marquess of Northampton, P.R.S., showing the phragmocone, muscular mantle, and portions of the fleshy arms, preserved in their natural relative positions.

PLATE IV.

Fig. 1. The specimen from the collection of S. P. Pratt, Esq., F.R.S., showing the phragmocone, part of the muscular mantle, lateral fins and funnel.

c. The apex of the crushed and disturbed phragmocone.

d. Portions of the transverse muscular tunic of the mantle.

e, *e*. The two lateral fins: that on the right side is entire.

f. The remains of the infundibulum.

g. The levator muscles of the infundibulum.

m. The striated horny plate ascribed to the gizzard.

n. The remains of the ink-bag.

Fig. 2. Section of an embalmed Calamary (*Celæno*, Munster).

PLATE V.

The specimen from the collection of S. P. Pratt, Esq., F.R.S., showing the muscular mantle, head, and uncinated arms.

d. Portions of the transversely fibrous coat of the mantle, obscured in many parts by apparently the remains of the pigmental coat of the skin.

i. The uncinated arms.

l. The remains of the eyes.

m. The striated horny plate ascribed to the gizzard.

PLATE VI.

Fig. 1. The specimen from the collection of WILLIAM CUNNINGTON, Esq.

Fig. 2. A magnified view of one of the horny hooks.

Fig. 3. A magnified view of part of the head with the fibrous bodies supposed to belong to the eyes.

PLATE VII.

Highly magnified views of the spathose and muscular textures of the Belemnite.

Fig. 1. A portion of a transverse section of the fibrous guard.

γ. The lines indicating the prismatic fibres.

β. The lines indicating the layers of growth.

ε. The triangular specks produced by abrasion of the surface.

Fig. 2. Longitudinal section of the fibrous guard, across the prismatic fibres, δ.

Fig. 3. Primitive muscular fibres of the *Onychoteuthis Banksii*, showing transverse striæ, similarly magnified.

Fig. 4. Primitive muscular fibres of the *Belemnites Owenii* magnified 600 diameters, linear.

PLATE VIII.

Restoration of the Belemnite, according to the structures observed in the specimens preserved in the Oxford clay at Christian-Malford.

The same letters indicate the same parts as in the foregoing figures.

d'. The continuation of the mantle over the phragmocone and guard of the internal shell of the Belemnite.